

LEATHER INDUSTRIES
LABORATORY BOOK

LEATHER INDUSTRIES

LABORATORY BOOK

OF
ANALYTICAL AND EXPERIMENTAL METHODS

BY

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PREFACE

TO

THE SECOND EDITION.

THE following notes on Analytical Methods employed in Leather Manufacture were primarily intended mainly for the use of my own students, and merely to supplement verbal teaching; and although the scope of the book has been considerably expanded, it is occupied mainly with the practical details of analytical processes, and makes no attempt to teach either chemical theory, or the principles of leather manufacture. There is, of course, but little original in the methods described; but with scarcely an exception they have been carefully tested and found satisfactory in my own laboratory, and in many instances they have been modified to suit the special purposes for which they are employed. The present edition has been thoroughly revised, and many new methods added, which, it is hoped, will prove useful to the practical chemist.

My thanks are due to many of my friends for hints and suggestions received in the course of my work, but especially to Mr. J. T. WOOD for assistance in revision of the section on Ferments and Bacteriology.

HENRY R. PROCTER.

UNIVERSITY OF LEEDS,
1908.

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INTRODUCTION.

LEATHER manufacture has long been conducted by "rule of thumb," rather than by the more exact methods of modern science, not so much from any preference of manufacturers for the former, as because, from the inherent difficulties of the subject, the latter has been scarcely possible. Another obstacle which has somewhat impeded progress has been a misapprehension, perhaps justified in the past by adventurous inventors who would "revolutionise the trade," as to the part which chemistry is destined to play in the tanning of the future. The term "chemical tanning" became one of reproach and contempt; and it has been too much forgotten that in every tan-yard, chemical processes are being carried on of a complexity so great that as yet they are very imperfectly understood, even by those chemists who have devoted themselves most thoroughly to the task.

The first service which chemistry must render to the trade is not to supersede the processes of manufacture which have stood the test of experience, but to explain the principles on which they depend, and so enable us to carry them out with more exactness and invariable success. To do this, we must apply the usual tools of chemical research—the balance and the measure; but to do it successfully, methods have to be elaborated to determine the nature and quantities of the very varied constituents of all the materials used. In this direction there is yet much to be done, but it has been my effort in this little book to sum up the best methods which are yet known, and to put them in a handy form for use and reference. Those who can look back on the progress of the last twenty years will feel that,

however much remains to be done, the progress already made has been very substantial. It is now possible to determine the strength and value of most tanning materials with an accuracy and certainty which then was quite unknown; waste liquors and tans can be analysed with approximate accuracy, and the loss in leaching and tanning ascertained, and many new methods have been introduced for the control of processes and materials; and only the systematic application of these methods is required to learn much which we yet need to know about the economies of the tanning process. In liming, bating and drenching, much information has been gained as to the losses of hide substance which take place, and the way in which these are influenced by the materials employed, and the mode in which the process is conducted; and new materials have been introduced and accepted by the trade, for which means of valuation and analysis have been devised. Bacteriology has taught us at least some of the methods by which fermentative processes such as puering and drenching can be regulated, and has strengthened the hope that we may be made independent of the old and disgusting materials; while the removal of lime by purely chemical means is perfectly understood, and a matter of every-day practice to many tanners. In the tan-house we no longer hear the vague talk about "gallic acid" as an enemy to be avoided, but the amounts of acetic and lactic acid in the liquors are estimated in well-managed sole-leather yards as a matter of routine; their influence on the proper tanning of the goods is well understood; and it is recognised that they are derived, not from the destruction of tannin, but from the sugary matters of the tanning materials.

In chrome tanning an entirely new process originating in the laboratory has firmly established itself, and is still finding new applications; and the accuracy which is essential to its success has involved the invention of new schemes of analysis, and done much to familiarise tanners with chemical methods.

In the analysis of oils and fats, the old and unreliable tests have been largely superseded by new and exact methods; and

INTRODUCTION.

tanners rather than chemists must now be blamed that more is not known of the differences of constitution which render an oil fit or unfit for the purposes of the trade ; since, when difficulties arise, the chemist is constantly told that the source of the materials in fault cannot be traced, and that no samples have been preserved for analysis !

In dyeing and staining, the old natural dyes are more and more giving place to the synthetical organic colours of the chemist, which compete with them successfully, not only in price but in brilliancy and fastness. Here, again, the services of the chemist are in demand, not only to test the qualities of the dyes, but to match the tints required with the cheapest combinations, and to recognise the character of unknown colours.

In one way, indeed, chemistry must be admittedly unwelcome to the conservative tanner—it is the key to mysteries ; and has rediscovered and thrown open to the world many secrets which he believed safely locked within the doors of his factory ! But even so it must be reckoned with, for, like the genii of the stories, it can neither be killed nor bound, but is fortunately the willing servant of all who have intelligence to use it ; and as capable of discovering new secrets as of throwing open the old ones.

A few words may here be said as to the origin and scope of the succeeding chapters. They originally, in a much briefer form, were a part of the Author's 'Text-Book of Tanning,' published in 1887 ; but as time went on, and knowledge increased, it became evident that the amount of analytical chemistry available and earnestly demanded by the more advanced workers was too large to be conveniently incorporated in a book intended rather for the tannery than for the laboratory ; while, on the other hand, the technical chemist would have had difficulty in picking out the methods he required from the larger volume. On these accounts, it was decided to issue the purely laboratory matter in an independent volume, which has now come to its second edition, and the reader may be referred for information on the theory and practice of leather manufacture to the 'Principles of Leather Manufacture,' which has appeared as a

separate volume; * while, on the other hand, the working details of chemical methods of research are given in the 'Laboratory Book' and merely referred to in the 'Principles.'

The 'Laboratory Book' is not intended to take the place of the ordinary chemical text-books, but to supplement them; and those readers who have not already a knowledge of the common methods of the laboratory will find it needful to study some of the many Manuals on general Quantitative Analysis. It is also extremely desirable that the chemist should familiarise himself with some of the later developments of chemical theory such as the laws of chemical equilibria and mass-action, of ionic dissociation, and of osmotic pressure; and the advances which are now being made in our knowledge of colloidal solutions which have important bearing on the very complex problems of leather manufacture. To those who have already some knowledge of the analytical methods, it is hoped that the opening section on 'General Chemical Methods' may prove a useful reminder of the more important details of manipulation. The succeeding chapters assume a knowledge of these, and of the elements both of leather manufacture and chemical theory.

* E. & F. N. Spon, Limited, price 18s. net.

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SECTION I.

GENERAL METHODS.

THE object of chemical analysis is to divide a material into its constituent parts, so that they may be weighed or measured, and their proportions calculated. These are generally expressed as percentages of the whole, and are calculated by multiplying the weight found by 100, and dividing by the original weight of material used. It is rarely necessary or desirable to go beyond the first place of decimals in technical analyses. Sometimes the weight of the substance which it is desired to estimate is not found directly, but calculated from that of some other substance to which it is known to be proportional.

Weighing.—Substances must never be weighed directly in the balance pan, but always in a basin or some other vessel, of which the weight is previously determined, and which must be dry, cool, and clean, and must not be touched by hot or damp fingers before weighing. Vessels which have been heated, especially if they contain substances which absorb moisture readily, must be allowed to cool in the "desiccator" or "exsiccator," a vessel with an air-tight cover, and usually containing dry calcium chloride or sodium hydrate, or pumice moistened with concentrated sulphuric acid. It must be placed on the pan while the balance is arrested, and neither vessel nor weights must ever be touched while the beam is free. Weights are placed on the right-hand pan with forceps, beginning with the largest, and trying each in turn by liberating the balance, till one is found

which is lighter than the body which is to be weighed. Smaller weights are then added in the same way, always trying the larger first, and keeping the weight below that of the object. When the weight is within one centigram, the balance case is closed, and the final adjustment is made with the rider. This is complete when the index swings an equal distance on each side of the centre. Many balances are adjusted to swing an even number of divisions to one side or the other for each milligram of over or under-weight, and most can be made to do so by

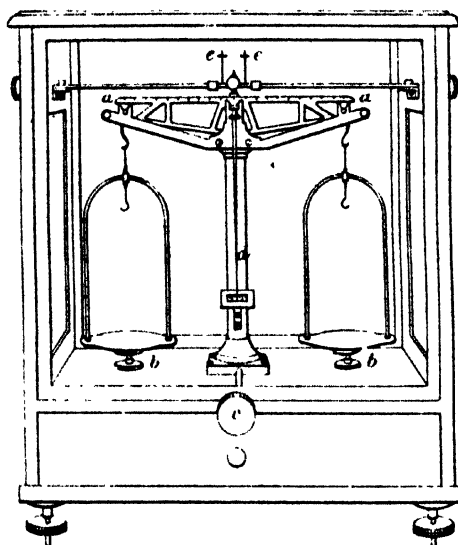


FIG. 1.—CHEMICAL BALANCE.

a, scale for rider ; *b*, arrestment for pans ; *c*, *e*, arms for moving ride

suitable adjustment. Where this is the case the division at which the pointer turns at each side is noted and that to the left deducted from that to the right, and the corresponding number of milligrams + or -, added to the weight on the pan. It is generally safest to confirm the result by moving the rider to the weight indicated. The balance may be made to oscillate if required by gentle fanning with the hand. The weight should be read off the empty spaces in the box, and entered in the notebook, and checked in taking off the weights.

Measuring is done in glass vessels marked to definite quantities. Water, and all other liquids which wet glass, form a hollow upper surface or meniscus, the lowest part of which must be brought level with the mark. This is most accurately done by looking through the liquid at some distant light object nearly level with the eye, the lower surface of the meniscus being darkened, if necessary, by holding some dark object behind

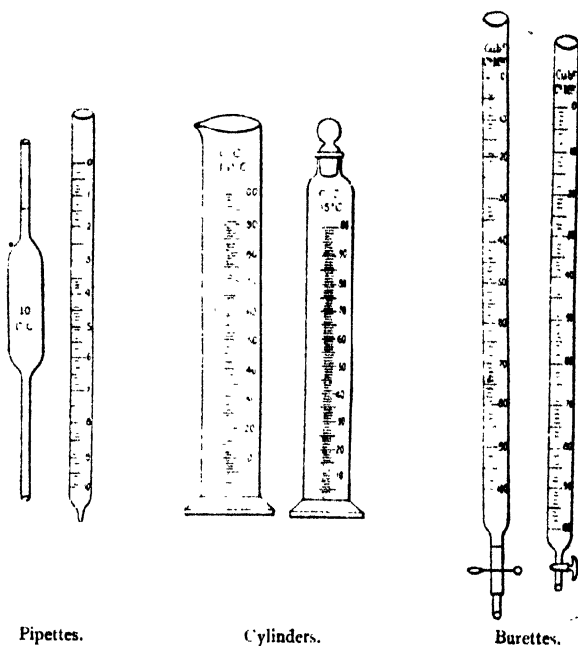


FIG. 2.—MEASURING INSTRUMENTS.

and slightly below it. A less accurate method is to look at the lower edge of a white card held behind and nearly level with the meniscus, with which the eye must also be level. For dark-coloured liquids in burettes, a Mohr's float should be used, which may be either of glass or porcelain. Care must be taken that the vessel is upright while reading. Flasks and cylinders are usually graduated to *contain* the amount to which they are marked; pipettes and burettes to *deliver*; hence, if the former

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are used for delivery, the amount of liquid which clings to the sides must be determined and allowed for. Burettes must not be read till time has been allowed for this to run down,* and pipettes must be drained against the side of the vessel, but not blown out. The capacity of a vessel may be determined by weighing the amount of water at 15° C. which it contains (or delivers), when each gram corresponds to a cubic centimeter (c.c.).* Both flasks and pipettes are frequently inaccurately marked, and should be tested before use. The capacity of the lower divisions of burettes is often less than that of the upper ones. Pipettes are filled by sucking till the liquid rises above the mark, quickly placing the forefinger on the top, and allowing to run down till the mark is reached. Ordinary pipettes should not be used in the mouth for very poisonous or corrosive liquids, but may be sucked through a bulb tube connected with rubber tubing which is pinched when the pipette is full.

Marking Vessels.—Glass is best marked with a writing diamond, or by etching with hydrofluoric acid. The latter is most easily done by covering with a thin film of beeswax or solid paraffin, and etching with a needle. The etched part is then covered for a few minutes with a piece of blotting paper moistened with liquid hydrofluoric acid. The latter must be handled with great care as it is extremely corrosive. Inks containing fluorides are sold for writing on glass. Porcelain basins and crucibles may be marked in common ink, dried and heated, first gently and then strongly in the oxidising flame of the blowpipe.

The Metric System.—As the metric system is now almost universally employed by chemists from its great convenience for purposes of calculation, and is likely ultimately to be also used by all civilised nations for commercial purposes, no apology is needed for its adoption in this book; but a few words on its relations with the antiquated weights and measures still used in England are perhaps necessary.

Metric weights and measures form a connected system related to the meter, a measure of length equal to 39.370113 English

* Laboratory vessels are generally graduated at this temperature, but the true liter is 1 kilogram of water at 4° C. Compare p. 5. Glass-tapped burettes are generally to be preferred to those with india-rubber tube and pinch-cock, but the tap should be lubricated with a little vaseline, and removed and washed after use with caustic alkalis, or it will stick.

GENERAL METHODS.

inches, which is approximately $1/10,000,000$ of the earth's quadrant measured from pole to equator. The meter is divided into 10 parts, or decimeters, 100 parts, or centimeters, and 1000 parts or millimeters. The standard of capacity is the cubic decimeter, or "liter," which of course contains 1000 cubic centimeters, or c.c. The standard of weight is that of 1 c.c. of water at 4° C. (the temperature of the greatest density of water), the weight of which is called 1 gram. Multiples of this are denoted by Greek numerals, thus :—

- 1 dekagram = 10 grams. ("Deka")
- 1 hectogram = 100 grams.
- 1 kilogram = 1000 grams, the weight of 1 liter of water.

In the same way fractions of 1 gram are denoted by Latin numerals, thus :—

- 1 decigram = 0.1 gram.
- 1 centigram = 0.01 gram.
- 1 milligram = 0.001 gram.

For purposes of reduction the following approximate numbers may generally be used :—

- 1 gram = 15.43 grains.
- 1 lb. av. = 453.6 grams.
- 1 liter = 0.22 gallon
- 1 gallon = 4.546 liters.
- 1 cubic meter of water weighs 1000 kilograms,
or 2200 lb., or approximately 1 ton.
- 1 liter = 61.02 cubic inches.
- 1 fluid oz. = 28.34 c.c.
- 1 meter = 39.37 inches.
- 1 inch = 25.4 millimeters.

Actual reductions may, however, in most cases be avoided by treating a question as one of proportion. Thus, 1 grm. or c.c. per liter is equivalent to 1 lb. or $\frac{1}{4}$ pint per 100 gallons, or very approximately to 1 oz. per cubic foot; 100 gallons of water weighing 1000 lb., and 1 cubic foot 997 oz.

For laboratory use, "Mohr's liter," which is the volume of 1000 grm. of water at 15° C. (59° F.), or ordinary laboratory temperature, is usually employed in place of the true liter, which is the volume of 1000 grm. at 4° C.

* The small difference between 1 gallon measured in liters, and 10 lb. avoirdupois measured in grams, is due to the different standard temperatures of the two systems. Consequently 1 gallon would only contain 4.536 "Mohr's liters."

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Thermometer Scales.—The Centigrade, or Celsius thermometer, in which the freezing point of water is taken at 0° and the interval between freezing and boiling point is divided into 100 parts or degrees, is to be preferred to that of Fahrenheit, which starts from an arbitrary zero, and in which freezing point is represented by 32° and boiling by 212° .

Centigrade degrees may be converted into Fahrenheit by multiplying by $\frac{9}{5}$ and adding 32. The following table gives the points at which they agree without fractions:—

Degrees Cent.	Degrees Fahr.	Degrees Cent.	Degrees Fahr.
—20	—4	45	113
—15	5	50	122
—10	14	55	131
—5	23	60	140
0	32	65	149
5	41	70	158
10	50	75	167
15	59	80	176
20	68	85	185
25	77	90	194
30	86	95	203
35	95	100	212
40	104	105	221

Réaumur's thermometer, which divides the interval between the boiling and freezing points of water into 80° is still a good deal used in Germany.

Specific Gravity is the weight of any body as compared to that of an equal volume of water. Thus, 1 c.c. of sulphuric acid weighs 1.84 grm., while 1 c.c. of water only weighs 1 grm.; the specific gravity of the acid is therefore 1.84. As bodies expand by heat, a uniform temperature must be adopted, which is generally 15° or 15.5° C. (59° or 60° F.). Liquids are brought to the required temperature by immersing the containing vessel in warm or cold water.

Liquids may be weighed in a flask or bottle carefully filled to a mark in the neck, or more readily in one provided with a perforated stopper (*pycnometer*). The flask is weighed first empty

GENERAL METHODS.

and dry, then filled with water, and finally with the liquid of which the specific gravity is to be taken. The weight of the liquid divided by that of the water (deducting the weight of the flask in each case), gives the sp. gr. To fill, place the flask on a saucer, fill quite full, insert stopper firmly and wash with cold water, or in the case of oils and fats, with petroleum spirit or benzoline, or other fat solvent, finally drying with a clean cloth. With thick liquids, such as extracts and viscid oils, a wide-necked flask, and a short wide funnel must be used in filling, and great care taken to avoid air-bubbles. Air-bubbles may also be removed by keeping the flask for some time in an exhausted air-pump receiver. Immediately after weighing the stopper must be withdrawn, and after returning as much of the extract to the sample as possible, the flask must be washed out with hot water, or, in the case of fats, with a suitable fat-solvent, and dried ready for use when wanted. For small quantities of liquid, the Sprengel tube, Fig. 3, is useful. It is filled through A by suction, and the liquid adjusted to mark M by applying blotting-paper to A to remove, or a glass rod with a drop to replace liquid.

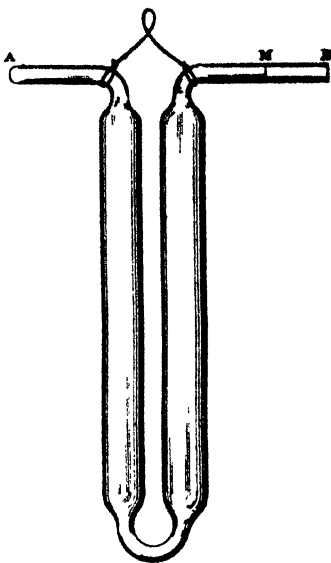


FIG. 3.—SPRENGEL TUBE.

A. and B. should not exceed about 1 mm. in internal diameter.

Solids, or very pasty extracts, may be determined by placing any convenient quantity in the flask, weighing, filling up with water, and weighing again. Deducting the weight of water so added from the total the empty flask would contain, the remainder is the weight of water which would occupy the same space as the solid, and which divided into the weight of the latter gives its sp. gr. Solid fats may be melted and allowed to solidify in the flask, but 18 to 24 hours should be allowed before filling with water and weighing, as fats only slowly regain their

original density after fusion. On the use of sp. gr. in water for determining dry solids in wet hide, see p. 99. Solids may also be determined by suspending by a fine wire from the hook above the balance pan, and weighing first in air, and then in water contained in a beaker supported on a bridge over the pan, resting on the bottom of the balance case. The last weight deducted from the first gives that of the water which has been displaced. If a solid of known weight in air, such as a glass plummet, be weighed first in water, and then in some other liquid, supported on the bridge, the loss of weight in the last case, divided by that in the first, will give the sp. gr. of the liquid. Special balances on the principle of the steelyard are often used for the purpose.

Specific gravities of liquids are rapidly taken with tolerable accuracy by hydrometers, which sink till they displace a volume of liquid equal to their own weight. Many of these are graduated for special purposes or have quite arbitrary scales. The degrees of the barkometer may be reduced to sp. gr. by dividing by 1000 and adding 1, but are rarely quite accurate. Degrees Twaddell may be similarly reduced by dividing by 200 and adding 1 (hence 1° Twaddell equals 5° barkometer). Baumé degrees are quite arbitrary, and can only be reduced by tables, of which several discrepant ones exist. The following so-called "Rational" scale is one very frequently used; but the use of this and other arbitrary and unscientific scales is to be avoided as far as possible:—

BAUMÉ HYDROMETER TABLE.

Baumé, 12° 5° C.	Sp. gr.	Baumé, 12° 5° C.	Sp. gr.
0	1·0000	40	1·3834
5	1·0358	45	1·4531
10	1·0745	50	1·5301
15	1·1160	55	1·6158
20	1·1608	60	1·7116
25	1·2095	65	1·8195
30	1·2624	70	1·909
35	1·3202	72	1·960

In taking a specific gravity with a hydrometer, the jar should be placed in a saucer and filled to the brim. Froth is then swept off with a glass rod, and the hydrometer put in, overflowing liquid being caught by the saucer. The hydrometer is read from the point where the curved surface of the water touches the stem.

GENERAL METHODS.

Evaporation is a general method of separating water and other volatile matter from non-volatile. It is most safely done in the water or steam-bath, but where large quantities have to be evaporated it is sometimes best to use a small flame. Liquids evaporate rapidly at or near boiling-point in broad shallow basins freely exposed to the air, or may be boiled in a lask with a funnel or glass bulb in the neck, or in a deep beaker covered with a clock-glass to avoid spurting, or in many cases, simply in a long-necked (Jena) flask. Tanning liquors may be concentrated in a flask as described without very material loss of tannin, but, like other materials which are injured by heat, are best evaporated *in vacuo*, the boiling point being much lower under reduced pressure. Many substances apparently dry, as bark, leather, and the residues after evaporation on the water-bath, may be thoroughly dried in the water-oven, which, being surrounded by boiling water and steam, is at nearly 100°C . Some substances part with water of crystallisation or hydration at 100°C ., but may often be dried without decomposition at ordinary temperatures over sulphuric acid, and, preferably, *in vacuo*. In many cases an air-oven may be used with advantage, heated by gas to 105° or 110°C ., in which the drying is much more rapid; but care must be taken that the temperature inside the oven is uniform and steady. To estimate water, a portion of the substance must be weighed in a basin or crucible, dried as above, and re-weighed, when the loss may in most cases be calculated as water. As most substances when thoroughly dried will absorb water from the air, the basin must be cooled in the desiccator, rapidly weighed, and again dried and weighed till the weight is constant. Inorganic matters can generally be dried at a much higher temperature, or even ignited, though other volatile matters will, of course, be included.

Distillation is merely a case of evaporation in which the volatile portion is collected. The liquid is placed in a flask, which is closed by a perforated cork fitted with a tube bent to an angle somewhat more acute than a right-angle, and fitting tightly into an inclined condenser consisting of a rather wide glass tube surrounded by an outer casing, through which cold water is allowed to flow from a tap. The lower end of the condenser tube passes into a flask, with which it should form a pretty close, but not an air-tight, connection, and which, in the

case of volatile liquids, should also be immersed in cold water or even in ice. The liquid in the flask is boiled, either by a flame or on a sand-bath, or, in the case of combustible liquids like alcohol or ethers, by immersion in a water* or steam-bath; and the vapours pass into the condenser, where they are cooled and condensed, and flow down into the receiving flask.

This simple arrangement is quite satisfactory where mere purification of a liquid from non-volatile impurities is all that is required; but where a more volatile liquid must be separated from one of higher boiling-point, as for instance alcohol from water, it does not prove very effective, as a portion of both liquids is carried over, though in simple cases it will act fairly well. It is usually necessary to know the temperature of the vapour which is being distilled, in order to judge when the process has gone far enough, for which purpose a second hole is made in the cork of the distilling flask, and the bulb of a thermometer is introduced into the neck of the flask. A more convenient arrangement is to use a "distilling flask" in which a side tube passing into the condenser is fused into the neck, while the thermometer is fitted through the cork, with its bulb near the opening of the side tube. The most difficult case is that of a liquid like petroleum, which consists of a mixture of a great number of different hydrocarbons of different boiling-points, which it is desired to separate. When such a liquid is boiled, the fractions of higher boiling-point distil first, but the vapour, even from the outset, consists not merely of the most volatile, but of a mixture of these and a smaller proportion of the less volatile. The separation is greatly facilitated by the use of a "dephlegmating" or "fractionating" tube, in which the less volatile vapours become condensed, and drop back into the distilling flask, at the same time washing the ascending vapours and giving up to them any more volatile portions. Glynsky's and Le Bel Henniger's are, perhaps, the best forms of this apparatus, but a wide tube filled with large glass beads or short lengths of quik tubing, and fitted with a side tube, is also very effective. The arrangement is shown in Fig. 4. Even with a fractionating tube the separation of the different liquids is rarely complete; but by separating into portions boiling, say, from 60° to 70°, 70° to 80°, and so on, and

* Higher temperatures may be obtained by the use of calcium chloride solution, or by glycerine or oil baths.

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again fractionating these portions separately, nearly pure products may be obtained. Instances of the application of this method may be found in the separation of alcohols and volatile acids of the acetic series, and of petroleum ether.

Ignition.—Heating to redness in an open vessel drives off chemically combined water, ammonia, and often carbonic acid, etc., and destroys most organic matter. This is generally best done in platinum vessels, but salts of tin, lead, copper and other metals easily reduced to the metallic state, must not be heated

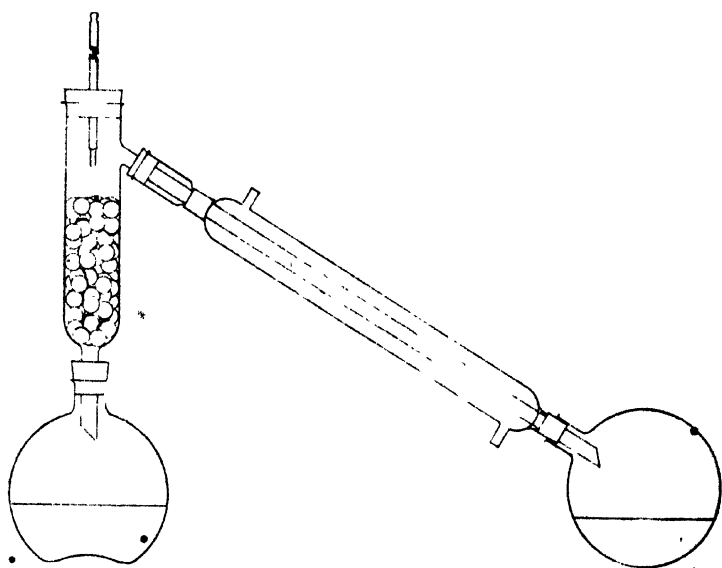


FIG. 4.

in platinum, or the vessel may be destroyed. Materials containing chlorides, or other salts fusible at a red heat, must be ignited *very* gently and slowly, or the particles of carbon will be encased and escape combustion. If this occurs, the addition of a little water when cool, with subsequent drying on water-bath and re-ignition will often succeed in completing combustion. In difficult cases the ash may be moistened with solution of ammonium nitrate, and again dried and ignited, or the soluble salts may be extracted with water from the charred mass, which is collected on a quantitative filter-paper, returned to the crucible and com-

pletely burnt, and the solution evaporated with the ash after ignition.

Precipitation.—Many substances soluble in water, etc., can be converted into insoluble compounds, and so separated by precipitation. Thus, on addition of BaCl_2 , sulphuric acid (free or combined with bases) is precipitated as insoluble BaSO_4 ; and ammonium oxalate precipitates all soluble lime salts from neutral or alkaline solution as calcium oxalate, which may be converted into carbonate by gentle ignition, or into quicklime (CaO) by strong ignition over the blow-pipe. Precipitation is mostly aided by warmth and time, and often delayed or prevented by presence of organic matter. It is generally rendered more complete by an excess of the precipitant. Very finely divided precipitates, such as calcium oxalate, usually become coarser by boiling, or standing for some time in the liquid in a warm place, and are then more easily filtered and washed.

Filtration.—Precipitates are separated from liquids in which they are suspended by settling and filtration. Circles of paper are used, as filters, which are folded in four, one fold opened, and inserted in a funnel, which must be slightly larger than the cone of paper. The filter must generally be wetted with distilled water, except when dry filters are required for solutions for volumetric analyses. This water must be allowed to run through the filter, so that the upper part of the funnel is not wetted. Special filter paper is used for quantitative work, which leaves no appreciable ash on ignition. With bulky or gelatinous precipitates it is often convenient to use the vacuum pump where one is available. When this is not the case, filtration may be much quickened by the use of a piece of small glass tube below the funnel, attached with a piece of indiarubber tube as in Fig. 5. The moistened filter must be closely fitted to the funnel by gentle pressure round the edge, especially at the fold.



FIG. 5.

Washing Precipitates.—Before filtration, it is generally best to let the precipitate settle, and pour first the clear liquid on the filter; and if the precipitate is heavy and settles well, water may be added, and the settling and decantation repeated several times. The liquid should be poured down a glass

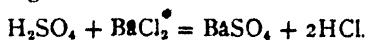
GENERAL METHODS.

rod on to the side of the filter, avoiding spurting, and the last traces of precipitate removed from the beaker by rubbing with a cap of rubber tube on the end of the glass rod, and rinsing with a stream of water from the fine jet of the wash-bottle. A short glass rod, bent at somewhat more than a right angle, and hung on the edge of the beaker, is often convenient for pouring and does not disturb the precipitate. The precipitate must be well washed on the filter, which is generally best done with hot water blown on it in a thin stream from the wash-bottle. The filter should be allowed to run dry each time before adding more water. If the precipitate is subsequently to be removed from the paper, it is desirable to wash it as completely down to the bottom as possible.

Drying Precipitates.—Organic precipitates must be collected on filters previously dried till constant in the oven, and weighed in a closed tube or weighing bottle. The filter with precipitate is similarly dried, weighed, and the weight of the filter deducted. Instead of weighing the dried filter, it may be balanced by a second which is dried with the precipitate and used to ascertain the tare.

Mineral precipitates may generally be ignited. A crucible previously dried and weighed is placed on glazed black paper, and most of the precipitate is separated from the filter-paper and transferred to the crucible. The filter-paper is now folded up small, twisted in a platinum wire, and carefully burnt in a Bunsen flame over the crucible, into which the ash is shaken, and the whole then ignited, cooled in the desiccator and weighed. A deduction must be made for the filter ash if appreciable, but with modern papers it may generally be neglected. Where no reduction is to be feared, precipitates may be ignited with the paper in the crucible.

Calculation of Results.—In many cases the substance actually weighed is not that of which we require the weight, but some other compound, from which the weight must be calculated. Thus sulphuric acid is generally weighed as barium sulphate, the reaction being as follows :—



The atomic weights are $98 + 208 = 233 + 73$, and are obtained by adding the atomic weights of the constituents of each body

Thus in this case we reckon only 98 parts of sulphuric acid for every 233 parts of barium sulphate weighed. Where many analyses are made, it is convenient to use factors to give the actual weight by simple multiplication. Tables of such factors and their logarithms are given in the Chemiker Kalender and many text-books.*

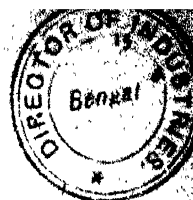
Volumetric Analysis.—It is clear that if we know the weight of BaCl_2 required for the above reaction, we can calculate that of all the other substances, and *vice versa*. If we have a solution of BaCl_2 containing exactly 104 grm. per liter, or 0.104 grm. per c.c., and if for instance it requires 20 c.c. to precipitate all the sulphuric acid (free or as sulphates) in a liter of water, we can calculate that the water contains 20×0.049 or 0.98 grm. of sulphuric acid per liter. Such solutions of known strength as that of barium chloride are known as "standard solutions" and are usually made to contain 1 combining weight of the substance in grams per liter, or some definite fraction of it. Referring to the equation, it will be noted that 1 eq. of H_2SO_4 liberates 2 eq. of HCl , and that the 1 atom of Ba in the barium sulphate takes the place of 2 atoms of hydrogen. Such elements are called "divalent," and acids which, like sulphuric, have 2 atoms of hydrogen which can be displaced by one divalent atom are called "dibasic." In making "standard" solutions of such substances, it is found convenient, in order to make them correspond with those of monovalent compounds like hydrochloric acid or sodium hydrate, to take only *half* their atomic weight in grams per liter, or in general terms, such a quantity as will react with 1 monovalent atom such as H, Na, or Cl. Such solutions are called *normal* or *N/1* solutions. Solutions of one-tenth this strength are called *decinormal* or *N/10*.

TABLE GIVING THE QUANTITY OF THE FOLLOWING SUBSTANCES (CONTAINED IN, OR EQUIVALENT TO, 1 LITER OF N/1 OR 10 LITERS OF N/10 SOLUTION.

Sulphuric acid . . .	H_2SO_4	$\frac{1}{2}$ mol .	49.0 grm. (= 48 grm. SO_3).
Hydrochloric acid . .	HCl	1 " =	36.5 " (= 35.5 grm. Cl).
Nitric acid . . .	HNO_3	1 " =	63.0 "
Sulphurous acid . . .	H_2SO_3	$\frac{1}{2}$ " =	41.0 "
Oxalic acid . . .	$\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{Aq}$	$\frac{1}{2}$ " =	63.0 "

* Küster's "Logarithmische Rechentafeln für Chemiker," Beit and Co., Leipzig, is very complete. The use of the slide-rule saves much time in calculation, and is mostly sufficiently exact.

GENERAL METHODS.



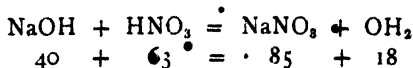
Formic acid . . .	HCOOH	1 mol.	=	46.0	gm.	
Acetic acid . . .	CH ₃ COOH	1	"	=	60.0	"
Lactic acid . . .	C ₃ H ₅ OH.COOH	1	"	=	90.0	"
Sodium hydrate . .	NaOH	1	"	=	40.0	"
Sodium carbonate (anhydrous)*	Na ₂ CO ₃	½	"	=	53.0	"
Sodium carbonate (crystallised).	Na ₂ CO ₃ . 10Aq	½	"	=	143.0	"
Potassium hydrate .	KOH	1	"	=	56.1	"
Magnesia . . .	MgO	½	"	=	40.2	(insoluble).
Baryta . . .	BaO	½	"	=	76.7	(sol. 2.89 p.c. at 15°).
Barium hydrate . .	Ba(OH) ₂ . 8Aq	½	"	=	157.7	"
Barium chloride . .	BaCl ₂ . 2Aq	½	"	=	122.1	"
Calcium oxide (lime)	CaO	½	"	=	28.1	(sol. 0.12 p.c.).
Calcium hydrate . .	Ca(OH) ₂	½	"	=	37.1	"
Calcium carbonate .	CaCO ₃	½	"	=	50.0	(insoluble).
Ammonia . . .	NH ₃	1	"	=	17.0	(= 14 N).
Zinc . . .	Zn	½	"	=	32.7	"
Silver nitrate . .	AgNO ₃	1	"	=	170.0	(= 35.5 Cl).
Potassium permanganate.	KMnO ₄	½	"	=	31.6	As oxidising agents.
Potassium bichromate	K ₂ Cr ₂ O ₇	½	"	=	49.0	Do.
Chromic "acid" (anhydride) . . }	CrO ₃	½	"	=	33.4	Do. { (CrO ₃ = 100.1) (Cr ₂ O ₃ = 152.2)
Iodine . . .	I	1	"	=	126.9	Do.
Bromine . . .	Br	1	"	=	80.0	Do.
Sodium thiosulphate	Na ₂ S ₂ O ₃ . 5Aq	1	"	=	248.2	in reducing I and Br.

These figures are corrected to the International Table of atomic weights, taking O = 16, but decimals less than 0.3 may for most practical purposes be disregarded, and in some cases the atomic weights themselves are uncertain to this extent.

SECTION II.

ALKALIMETRY.

ONE of the most important applications of volumetric analysis is the estimation of acids and bases which unite together to form salts. Thus nitric acid and sodium hydrate react to form the neutral salt sodium nitrate, according to the following equation:—



It is obvious that if the quantity of nitric acid necessary to combine with the whole of the soda is known, the amount of the

latter can be calculated, and *vice versa*. Since both free acids and free bases have marked properties which are not shared by their salts, the completion of the reaction can be determined with great accuracy, usually by the aid of "indicators," which are generally substances which show a marked colour-change on passing from the alkaline to the acid condition, or *vice versa*. According to the modern view, the acids owe their distinctive character as a class to the fact that in dilute solution they become partially dissociated into H and another "ion," differing with the acid, but in the case of nitric acid NO_3 . Similarly, the alkalis dissociate into the ions OH and the alkali-metal (or some group such as NH_4 which takes the place of a metal). Their "strength" or chemical activity depends on the extent to which they are dissociated or ionised in solution, the stronger acids and bases being so dissociated to the extent of about 90 per cent. in decinormal solution, while the weaker ones are dissociated very little, the extent of dissociation in all cases increasing with increasing dilution. Thus the acids owe their common properties of sourness, etc. to the presence of the ion H in their solutions, and the bases to that of OH, and the most important point in the reaction of acids and bases is the combination of these two ions to form water, as shown in the equation, since the salts really remain dissociated in the solution, and only combine to form a single substance as the water is evaporated.*

Indicators are mostly weakly acid organic colouring matters, the salts of which have a markedly different colour from the free acid. (Weak colour-bases may also be employed, but are not so commonly useful.) In the presence of a stronger free acid, the salt of the acid colouring matter is decomposed, and the colour-acid liberated; and similarly in the case of basic indicators, the free base is liberated by a stronger base.

Methyl Orange (Helianthine, Tropæolin D) is the sodium or ammonium salt of dimethylamidazozenesulphonic acid $\text{C}_6\text{H}_4 \cdot \text{N}(\text{CH}_3)_2 \cdot \text{N} : \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{H}$. The free colour-acid is red (or in the solid form violet), and its salts are yellow, and their solutions change from yellow to red in the presence of an

* Those who are interested in the modern theory of salt-formation are referred to Ostwald's excellent little book, "Die Wissenschaftliche Grundlage der Analytischen Chemie" (Leipzig), or its English translation.

acid sufficiently strong to set the colour-acid free. As this acid is of medium strength, this change is only pronounced in the presence of the stronger mineral acids, and is scarcely affected by carbonic, boric, sulphydric, arsenious, silicic, oleic, stearic and many other weak inorganic and organic acids. Thus methyl orange is quite useless for the titration of even the stronger organic acids, such as acetic and lactic, with which it gives no definite end-reaction, and their influence is still further diminished in alcoholic solution, probably because of their diminished ionisation in this medium, and it is said that it may be used for titrating sulphuric or hydrochloric acids in the presence of free acetic, if a sufficiency of alcohol is added.* Except for such special purposes the presence of alcohol is to be avoided, as diminishing its sensitiveness. On the other hand, it is very suitable for titrating weak bases, giving sharp reactions with ammonia, and with most of the alkaloids. The presence of neutral salts, and even of chlorides, sulphates and nitrates diminish the sharpness of the colour-change, and should be avoided as far as possible. Many salts of dibasic and tribasic acids are alkaline to methyl orange which are neutral to phenolphthalein; and thus by the use of both indicators, bicarbonates, normal carbonates, and indirectly caustic alkalies can be titrated in the same solution (p. 28), and sulphurous acid, bisulphites and sulphites in the presence of each other (p. 27). It is generally best used in the cold, and does not answer well in boiling solutions. It is destroyed by free nitrous acid.

An aqueous solution of 1 grm. per liter is most suitable for general use, of which not more than four or five drops should be used per 100 c.c. of solution titrated, as the end reaction is less sharp with larger quantities. When decinormal solutions are used, the volume required to set free even this quantity of colour-acid is quite appreciable, and for very exact work such as water analysis, an equal number of drops should be added to a similar volume of distilled water, and the amount of acid required to produce the colour-change noted, and deducted from that used in the actual titration, when the colour produced in the distilled water is matched by that in the liquid titrated.

Phenolphthalein is a much weaker acid than methyl orange,

In the Author's hands this method of titration has proved quite unreliable.

and is itself colourless, while its alkaline salts are intensely red. Hence it is extremely sensitive to weak acids, but only sharply affected by the strong bases, such as the alkalies and alkaline earths, and even ammonia gives with it no sharp end-reaction. Thus it is reddened by alkalies and alkaline carbonates, but not by hydric carbonates (bicarbonates), nor by the insoluble carbonates of the alkaline earths, nor by neutral sulphites, or salts of the fatty acids (soaps), and is useless with ammonia. In suitable cases, it is one of the most sensitive of indicators. It is best used in 1 per cent. alcoholic solution, of which two or three drops are required for titration in aqueous, and more in alcoholic solutions.

Litmus is less generally useful than the above, except as a convenient test in the form of red and blue papers. It is reddened by acids, blued by alkalies and alkaline carbonates, and turned an uncertain purple by carbonic acid, but can be used for the titration of carbonates in a boiling solution.

Lacmoid changes colour like litmus, and may be employed either as a 1 per cent. alcoholic solution or as red or blue papers. The papers may in almost all cases be used in place of methyl orange, being practically insensitive to carbonic and boric acids. The solution is more affected by these acids, but may be used with carbonates in boiling solution.

Congo Red is turned blue by acids. Its range of sensitiveness is very similar to methyl orange, though the change is less sudden. Notwithstanding this, it is sometimes useful by artificial light, or in liquids of which the colour makes methyl orange inapplicable. It may also be used in the form of test-papers.

Alizarin is a useful indicator in certain special cases, such as the estimation of hardness in water (p. 33), and yields a violet solution in presence of alkalies, turning very sharply to yellow on addition of acid. $\frac{1}{2}$ per cent. of the commercial paste diluted in water is a suitable strength for use.

Standard Solutions.—It is obvious from what has been already said that if we have a solution of any suitable acid of exactly known strength, we can determine that of any base by measuring the quantity required to neutralise it, or similarly we may start with a known solution of a base, and with it determine that of any acid; and, of course, by using the acid solution of which the strength is thus ascertained, we can determine that of

ALKALIMETRY.

any other base. Evidently, the substance selected as our starting point must be one not liable to change, and which can be exactly weighed, and which is of perfectly constant composition, and it is also desirable that it should be either a strong base, or a strong acid, since with these the indicators react most sharply. Many substances have been proposed for the purpose but of these, pure normal dry sodium carbonate is one of the most suitable, and it will be adopted in the following pages. Great pains should be taken to insure its absolute purity, since upon this depends the accuracy of all work done with the standard solutions prepared by its aid.

Solutions of any strength may be used in alkalimetry, so long as that strength is accurately known, and it was formerly customary to make special solutions for particular purposes, so that for example, 1 c.c. corresponded to 1 per cent. of the substance to be determined. Reasons have been given on p. 14 why it is generally more convenient that they should contain one combining equivalent of the substance weighed in grams in 1 liter of solution, or some definite fraction of this strength; and calculation can usually be avoided where many analyses have to be done, by weighing out a suitable quantity of the material of which the strength is to be determined.

Starting with sodium carbonate, we may either proceed to dissolve such a quantity as will make exactly 1 liter of "normal" strength, or we may use the dry carbonate in weighed portions to determine the exact strength of an acid solution, from which we can afterwards standardise any alkaline solutions required. The former is the simpler in theory, and shall be first described, but the latter will usually be found easier and more accurate in practice, and less liable to error.

Normal Sodium Carbonate Solution direct. About 60 grm. of purest anhydrous sodic carbonate is heated over a Bunsen burner till the bottom of the basin shows faint redness, and is cooled in the desiccator.* A weighed platinum or porcelain basin may be used. Weights to 53 grm. and the weight of the basin are now placed on the balance, and the basin is rapidly brought to within 0.01 grm. of the same weight by removing as

* A still more accurate method is to dry for some hours at 160° C. in an air-oven, but no appreciable quantity of carbonic acid is expelled by the method given in the text.

much of the sodic carbonate as is in excess.* A beaker with about half a liter of water is placed on a sheet of glazed black paper, and the sodic carbonate added little by little, constantly stirring with a glass rod till dissolved. The solution is poured into a liter flask, and the beaker repeatedly rinsed with distilled water, which is added to the flask till it is filled nearly to the mark. The temperature is then tested with a thermometer, and brought as accurately as possible to 15°C ., and the solution is made up exactly to the mark by water added from a pipette, and mixed in the flask as completely as possible, and finally poured into a clean dry stoppered bottle of somewhat more than one liter capacity, and shaken vigorously for five minutes.

Normal Hydrochloric Acid.—110 to 120 c.c. of the strongest hydrochloric acid is diluted to 1 liter, and well shaken in a stoppered bottle. A burette is filled with this dilute acid, 10 c.c. of the normal sodic carbonate is placed in a beaker, 2 drops of methyl orange solution is added, and then acid from the burette drop by drop till the solution just changes to orange; the solution being constantly stirred with a glass rod during the process. This is repeated several times, the acid being added rapidly to near the required quantity. The average of the readings is taken, and the number obtained multiplied by 100 gives the number of c.c. of the diluted acid required to make 1 liter. The quantity of distilled water required to make this up to 1000 c.c. is then accurately measured into a dry liter-flask, which is very carefully filled up to the mark with the dilute acid. After thorough mixing in a dry bottle, this should again be tested against the normal sodic carbonate, of which it should now neutralise an exactly equal quantity. The solutions should be kept at a temperature of 15°C . during the process.

In place of using an accurate sodium carbonate solution, an alternative method of fixing the strength of the standard acid is to fill a well-stoppered weighing bottle with hot and carefully

* To do this rapidly it must be done systematically. A portion of the material is removed on a spatula, and the remaining weight tested by releasing the balance. If still in excess, the portion on the spatula is rejected, and the process repeated till the weight on the balance proves less than that required. We now know that the true weight lies within the portion on the spatula, which is gradually shaken back till the weight is again in excess. The process is now repeated by removing a much smaller portion, with which a still closer approximation is reached; and so on until sufficient accuracy is obtained.

dried pure sodium carbonate, and after cooling in a desiccator, to shake out into a beaker a portion conveniently of about half a gram, of which the weight is determined by weighing the bottle before and after. This portion is dissolved in water, and titrated with the dilute acid of which the strength is to be determined; of which the number of c.c. required to make 1 liter of normal acid is found by multiplying the c.c. of acid used by 53, and dividing by weight of sodium carbonate taken. The average of several determinations which should agree very closely, is taken as correct, and is made up to a liter as above described. See also note, p. 40, for determination by silver nitrate.

Normal Sodium Carbonate from Hydrochloric Acid.—A solution of sodium carbonate somewhat over normal strength (say, 60 grm. per liter of ordinary air-dry anhydrous sodium carbonate or 160 grm. of pure soda crystals) is placed in the burette, and titrated upon 10 c.c. of the normal acid. The calculation is made precisely as in the case of standardising hydrochloric acid, the average of several determinations, multiplied by 100, giving the volume of the soda solution in cubic centimetres, which must be made up to 1 liter for a normal solution.

Normal Sodium or Potassium Hydrate, is made precisely as above by standardising against normal hydrochloric or sulphuric acid; 45 grm. of the purest NaOH, or 60 grm. of KOH being suitable quantities for 1 liter of the rough solution. To exclude carbonic acid, caustic standard solutions must be kept under petroleum oil (which should be previously well washed with soda solution, and afterwards with water); and when required for use, drawn off by a siphon passed through the cork of the bottle and fitted with a piece of rubber tube and a pinch-cock; or the cork may be tightly fitted with a tube filled with soda-lime, or absorption-bulbs with sodium hydrate solution to exclude carbonic acid.

Barium Hydrate, Calcium Hydrate.—Where absolutely caustic solutions are important, these may be usefully employed as their carbonates are insoluble, but they absorb carbonic acid and lose strength rapidly on exposure to the air. A saturated lime solution is only of about N/20 strength (cp. p. 54), and is often useful, as at a regular temperature it is practically of constant strength. Stronger solutions up to nearly normal strength may be made by the use of sugar solution (cp. pp. 54, 232). Barium

hydrate is much more soluble than calcium hydrate, a saturated solution being over N/3, so that any lower strength, such as N/5 can be easily prepared by dilution. If saturated solutions are employed, as they vary in strength with temperature, the quantity required should be filtered off immediately before use and the strength determined against standard acid. Supposing that 10 c.c. of N/10 acid require 12 c.c. of the barium hydrate solution and 10 c.c. of the unknown acid titrated requires 15 c.c., its value in N/10 acid is given at once by the proportion

$$12 : 15 = 10 \text{ c.c.} : 12.5 \text{ c.c.}$$

Normal Sulphuric Acid is made exactly as hydrochloric acid, but using only about 35 c.c. per liter of the concentrated acid (sp. gr. 1.840). The acid should be poured into the water, and not *vice versa*. It has the advantage that its solution can be boiled without loss by volatilisation.

Other Normal or Decinormal Acids can be similarly prepared, but in the case of organic acids, or the weaker mineral acids, phenolphthalein and caustic alkaline solutions must be used for standardising, instead of methyl orange and sodium carbonate. N/1 and N/10 oxalic acid may be made with considerable accuracy by dissolving 63 gm. or 6.3 gm. respectively of the purest recrystallised acid to 1 liter. Before weighing, the acid should be powdered, and allowed to dry for an hour or so exposed to the air at ordinary temperature. The solutions do not keep very well, and the normal solution will deposit crystals if cooled much below laboratory temperature.

Oxalic acid may be very approximately titrated with methyl orange, if a few drops of neutral CaCl_2 solution be added at the end of the titration to liberate hydrochloric acid by precipitation of calcium oxalate.

Decinormal Solutions may be made from the normal, by measuring 100 c.c. into a liter flask, and filling up with distilled water. It is well to verify after dilution against a solution of known accuracy, or a known weight of substance.

•*Testing of Commercial Materials.*—The following examples will give an idea of the use of alkalimetric methods in practical testing, but many other applications will suggest themselves to the chemist.

Sulphuric Acid.—10 gm. may be made up to 100 c.c. and

well mixed, and of this 10 c.c. may be tested with normal sodic hydrate or carbonate in presence of methyl orange. Each 1 c.c. of soda solution used corresponds to 0.049 grm. or 4.9 per cent. of H_2SO_4 . For most purposes, the strength may be ascertained from the specific gravity, as measured by a hydrometer or weighed in a specific gravity bottle by the use of the following table:—

SULPHURIC ACID. (*Lunge and Isler.*)

Specific Gravity 15° in vacuo.	H_2SO_4 per cent.	H_2SO_4 kilos. per liter.	Specific Gravity 15° in vacuo.	H_2SO_4 per cent.	H_2SO_4 kilos. per liter.
1.000	0.00	0.001	1.40	50.11	0.702
1.01	1.57	.016	1.45	55.03	.798
1.02	3.03	.031	1.50	59.70	.896
1.03	4.49	.046	1.55	64.26	.996
1.04	5.96	.062	1.60	68.51	1.096
1.05	7.37	.077	1.65	72.82	1.202
1.06	8.77	.093	1.70	77.17	1.312
1.07	10.19	.109	1.75	81.56	1.427
1.08	11.60	.125	1.80	86.00	1.564
1.09	12.99	.142	1.81	88.30	1.598
1.10	14.35	.158	1.82	90.05	1.639
1.15	20.91	.239	1.83	92.10	1.685
1.20	27.32	.328	1.84	95.60	1.759
1.25	33.43	.418	1.8415	97.70	1.799
1.30	39.19	.510	1.8385	99.95	1.838
1.35	44.82	.605			

Note.—The table is reckoned for the gravity of acid at 15°C ., compared to the (maximum) gravity of water at 4° . To calculate to water at 15° multiply by 1.000841—the difference may generally be neglected. It will be noted that the gravity varies very slowly with increasing strength as the acid approaches 100 per cent., and actually falls over 97.7 per cent., so that for very strong acid, gravity determination is of little value.

In order to calculate values for figures between those given in this and the following tables, it is generally sufficiently accurate to assume it as proportional to the difference between the next lower and the next higher value. Thus, if it be desired to know the strength of an acid of S.G. 1.525, the difference between that for 1.50 and 1.55 is 4.56, and the value required is $59.70 + 4.56 \times \frac{0.025}{0.050}$ or 61.98 per cent., the complete table giving 62.06.

Full and accurate tables for most acids and alkalies and many salts are given in the *Chemiker Kalender* published annually by Springer, Berlin.

Degrees of Twaddell's hydrometer may be reduced to specific gravity by multiplying by 0.005 and adding 1, thus $10^\circ \text{Tw.} = 1.050 \text{ sp. gr.}$

As tested by alkalimetry, it is quite possible for an acid to show over 100 per cent. H_2SO_4 from the presence of anhydride (SO_3) as in "fuming" or "Nordhausen" sulphuric acid, now often made by direct addition of anhydride.

The impurities of sulphuric acid most common and injurious for tanning purposes are iron and nitrous acid. Iron is detected on neutralising with soda or ammonia, when it falls as a yellowish precipitate, which may be recognised by the ordinary tests (p. 40). Nitric and nitrous acids are detected by pouring a strong solution of ferrous sulphate cautiously on the top of the strong cold acid in a test-tube held slanting, when a dark ring is formed at the junction of the two liquids. Sulphuric acid frequently contains arsenic in considerable quantities and sometimes other metals.

Hydrochloric Acid may be tested with soda solution like sulphuric. 1 c.c. of normal soda = 0.0365 gm. or 3.65 per cent. HCl. Its strength may also be calculated from the sp. gr. by the following table. It may be noted that degrees Twaddell correspond very approximately to the percentage of actual HCl. A yellow coloration of the acid generally indicates the presence of iron, which may be confirmed by the usual tests.

HYDROCHLORIC ACID. (*Lunge and Marchlewski.*)

Specific Gravity 15° in vacuo.	HCl per cent.	HCl kilos. per liter.	Specific Gravity 15° in vacuo.	HCl per cent.	HCl kilos. per liter.
1.000	0.16	0.0016	1.11	21.92	0.024
1.01	2.14	.022	1.12	23.82	.267
1.02	4.13	.042	1.13	25.75	.291
1.03	6.15	.064	1.14	27.66	.315
1.04	8.16	.085	1.15	29.57	.340
1.05	10.17	.107	1.16	31.52	.366
1.06	12.19	.129	1.17	33.46	.392
1.07	14.17	.152	1.18	35.39	.418
1.08	16.15	.174	1.19	37.23	.443
1.09	18.11	.197	1.195	38.16	.456
1.10	20.01	.220	1.200	39.11	.469

Crystallised Oxalic Acid $\left\{ \begin{array}{l} \text{COOH} \\ \text{COOH} \cdot 2\text{Aq} \end{array} \right\}$ should be pure white

and entirely soluble in distilled water. 6.3 grm. may be weighed out, and made up to 100 c.c. If 10 c.c. of the solution for a test be used, each c.c. of normal soda solution equals 10 per cent. or 0.063 grm. of pure crystallised acid, $C_2O_4H_2 + 2Aq$. The end-reaction with methyl orange is rendered sharper by the addition of a few drops of neutral calcium chloride towards the end of the titration ; but it is preferable to use caustic alkali and phenolphthalein.

Acetic Acid, $CH_3 \cdot COOH$, may be similarly determined, each c.c. of normal alkali being equivalent to 0.06 grm. of $C_2H_4O_2$, but caustic soda, or lime-water, and phenolphthalein should be used. Brown pyroligneous acid is difficult to test because of the dark compounds formed with soda, but may be indirectly determined by the quantity of marble, baric carbonate, or magnesia which it will dissolve.

Mineral acids in acetic acid, vinegar or other organic acid solutions may be detected and determined by adding excess of normal soda or sodium carbonate solution, igniting till the sodium salt of the organic acid is decomposed, and titrating back with N/1 acid, and methyl orange. Any loss of alkalinity is due to mineral acid since salts of all organic acids of the $RCOOH$ type leave carbonates on ignition (Hehner). Methyl orange is not reddened by acetic acid in presence of a sufficient quantity of alcohol, nor by small quantities of free acid in presence of acetates. The addition of alcohol does not prevent the action of the stronger acids, so that they can be titrated independently of acetic in a partially alcoholic solution.*

Formic Acid, $HCOOH$, is determined like acetic acid ; each c.c. of N/1 NaOH corresponding to 0.046 grm. of acid. It is now made synthetically by passing CO into soda-lime or concentrated KOH solution at $100^\circ C$. and subsequent decomposition of the formate by sulphuric acid. The commercial acid should contain about 65 per cent.

Lactic Acid, $C_3H_5OH \cdot COOH$, made by bacterial fermentation of starch or glucose, may be titrated in the cold with N/1 (or N/10) NaOH and phenolphthalein after dilution with water to about 10 per cent., 20 grm. of the ordinary commercial acid being made up to 100 c.c. and 50 c.c. titrated. The operation should be conducted as rapidly as possible, and the first perma-

* See note, p. 17.

nent pink shade taken as the end-point, to avoid acting on the lactic anhydride which is usually present. 1 c.c. of normal alkali corresponds to 0.090 grm. of lactic acid.

To determine the lactic anhydride, 25 c.c. of N/1 NaOH is added to the solution, neutralised as above, and the mixture is boiled for twenty minutes in a flask with reflux condenser or a long tube fitted in the cork to prevent loss of water. It is then titrated back with N/1 acid. Each c.c. of soda neutralised (or of acid less than 25 c.c. used) represents 0.081 grm. of lactic anhydride, or 0.090 of lactic acid existing in this form. Lactic anhydride is practically useless for the removal of lime or the swelling of hides. The boiling should not be prolonged beyond twenty minutes or other organic matters present may be acted on by the caustic alkali.

The only serious impurity for tanning purposes which is likely to be present is iron, which tends to injure the colour of the leather. Mineral ash may be determined by evaporating a known weight of the acid, first on the water-bath and then over a small flame with a cone of filter-paper inserted in the acid, and subsequently raising the temperature till the ash is free from carbon. The ash is then taken up with hydrochloric acid, evaporated (in porcelain basin) with a little nitric acid to small bulk, diluted with water to a known volume, and the iron is determined colorimetrically as described on p. 40. Sulphuric, oxalic and hydrochloric acids and their salts may be detected in the original solution by the usual reagents, and free mineral acids by evaporation to dryness with a measured excess of Na_2CO_3 solution, cautious ignition and subsequent titration of the sodium carbonate formed. Any deficiency will be due to the presence of free mineral acids, which are often present. Compare p. 367.

Boric (Boracic) Acid and Borates.—See p. 74.

Caustic alkalies may be estimated with N/1 or N/10, HCl or H_2SO_4 , using either methyl orange or phenolphthalein as indicators. 1 c.c. of N/1 acid corresponds to 0.040 grm. of NaOH or 0.0561 of KOH.

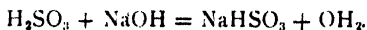
Ammonia may be similarly estimated, but methyl orange and not phenolphthalein must be used as indicator. Cp. p. 64.

Sodium and potassium may be estimated in carbonates, sulphides, borates and the salts of some other weak acids by the use of standard hydrochloric or sulphuric acid and methyl

orange, which is not at all affected by these weak acids. 1 c.c. of normal acid corresponds to 0.023 grm. Na and 0.0391 grm. K.

Sometimes by taking advantage of the different sensitiveness of methyl orange and phenolphthalein to acids and bases, it is possible to estimate a free acid or base and a salt at once in the same solution, as in the following instances.

Estimation of Sulphurous Acid and Sulphites.—It has been noted (p. 17) that bisulphites (hydric sulphites) are neutral to methyl orange and acid to phenolphthalein. If, therefore, both indicators be added to a solution containing free sulphurous acid and a bisulphite, and lime-water or N/10 caustic soda be added from a burette till the methyl orange becomes yellow, the whole of the free sulphurous acid will have been converted into bisulphite (half saturated with base), and each c.c. or N/10 alkali will equal one-tenth of a milligram-molecule of SO_2 , or 6.4 mgr., thus :—



If the standard solution be again added till the phenolphthalein becomes pink, the whole of the bisulphite, both that originally present and that formed from the free sulphurous acid, will be converted into neutral sulphite $\text{SO}(\text{NaO})_2$, and again each c.c. of N/10 soda used will equal 6.4 mgr., or one-tenth milligram-molecule of SO_2 present as bisulphite. Deducting from this an amount equal to that estimated as free acid, the bisulphite originally present is obtained. If the solution of sulphurous acid is at all a strong one, the titration must be done very rapidly in a narrow-necked flask to avoid loss by vaporisation, or the acid solution may be put in the burette and run into a known measure of caustic soda solution, when of course the order of the indications will be reversed.

If instead of a mixture of free acid and bisulphite, a mixture of hydric and neutral sulphite is to be estimated, the hydric sulphite may be first titrated with caustic soda as described, and then the resultant neutral sulphite titrated with methyl orange and N/10 hydrochloric acid till the latter is reddened. Each c.c. of N/10 acid will then be equivalent to 6.4 mgr. of the SO_2 present as neutral sulphite, from which that found as bisulphite must be deducted.

As an example, the following analysis of a sulphurous acid solution, which has been used for deliming, may be given, lime-water being used for titration.

10 c.c. of N/10 HCl = 21.3 c.c. lime-water.

10 c.c. sulphite liquor with methyl orange. } = 9.3 " " "

10 c.c. sulphite liquor with phenolphthalein. } = 20.2 " " "

Then

$$\frac{9.3 \times 6.4}{21.3} = 2.97 \text{ gm. per liter of SO}_2 \text{ free}$$

and

$$\frac{20.2 \times 6.4}{21.3} - 2.97 = 4.10 \text{ gm. per liter of SO}_2 \text{ as bisulphite.}$$

For other methods of estimation of sulphurous acid and sulphites, compare p. 73.

Hydrates, Carbonates and Bicarbonates of the alkalies may be estimated in a similar manner. Carbonates of the alkalies are alkaline, and bicarbonates neutral to phenolphthalein, and both are alkaline to methyl orange. Thus a mixture of alkaline carbonate and bicarbonate may be titrated in dilute solution by cautious addition of N/10 HCl or H₂SO₄ till the colour of phenolphthalein is discharged, when each equivalent of acid will equal two equivalents of base converted as under—



Acid is then added till methyl orange is reddened, and the whole acid consumed in both operations corresponds to the total base originally present in both forms. The result, however, is only accurate if the titration is done somewhat slowly and in dilute solution to prevent escape of carbonic acid. If a deep vessel is used, and a capillary tube attached to the burette is carried well below the surface, greater accuracy is obtained.

Another method is as follows. Alkaline earthy carbonates are alkaline to methyl orange, and neutral, especially after boiling, to phenolphthalein. This is applied to the analysis of lime, p. 54, and may also be utilised to determine caustic alkali in presence of carbonate in soda ash, etc. The solution to be tested is boiled with excess of neutral calcium (or barium)

chloride in a flask, converting the alkaline carbonate into chloride with production of insoluble calcium or barium carbonate, and is first titrated with HCl and phenolphthalein to determine the caustic alkali, and then with methyl orange for the carbonate.

In the latter titration it is convenient to add slight excess of acid, heat or digest for a short time to dissolve the carbonate, and titrate back with normal soda or sodic carbonate.

Alkaline Chromates are neutral to phenolphthalein,* while bichromates are acid. The latter may, therefore, be titrated with caustic soda in presence of the former. For details see p. 259.

In conclusion of this section, it may be pointed out that the possession of an accurate chemical balance is by no means necessary for many of the estimations just described. Standard solutions can be bought ready prepared, and from one accurate normal acid or alkali a great variety of other solutions can be adjusted by the use of measuring vessels only. 100 grm., or even $\frac{1}{4}$ lb. (= 113.4 grm.) of the material may be dissolved and made up to 1 liter, well mixed, and a measured quantity of the solution such as will bring it to the approximate strength required again diluted to 1 liter. Liquids, especially concentrated acids, which are awkward to weigh without proper appliances, may be measured, and either their strength per liter determined, or their weight calculated from their specific gravity. Thus 100 c.c. of sulphuric acid of 188° Tw. (S.G. 1.84) will weigh 184 grm., and, made up to 1 liter, will be about $3\frac{1}{4}$ times normal strength.

* The purest potassium chromate slightly reddens phenolphthalein in dilute solution, owing to hydrolytic dissociation; but this immediately disappears on the addition of a trace of acid or of bichromate, and its amount is too small to practically affect the accuracy of the titration. Similar effects are common with salts, either of weak acids or weak bases, though they are frequently overlooked.

SECTION III.

TECHNICAL WATER ANALYSIS.

THE analysis of water for technical purposes usually only extends to its mineral constituents, the traces of organic impurity which are important in potable waters, having but little effect on most chemical and technical uses. Bacteriological examination has received too little attention from the technical chemist, since there are many manufactures in which the presence of organised organisms is of an importance only second to that of their existence in drinking water; and some hints on this point are given in the section on bacteriology, p. 427. The "hardness" of water, on the whole, of the greatest manufacturing moment, but has been considered too exclusively from the point of view of the soap-maker, which often differs widely from that of other manufacturers; and although as an empirical method for determining the quantity of soap likely to be destroyed by a given water, the soap-test has its practical value, there are other and easier ways of ascertaining with much greater exactitude, what the actual qualitative and quantitative character of the hardness is. If no other fault existed in the soap-test than that it became practically useless in the presence of much magnesia, it would be sufficient to condemn it for general purposes, but when the somewhat indefinite character of the reagent, and the still more indefinite character of the reaction is considered, it becomes unnecessary to labour the subject. It is now possible, by simple volumetric methods, and with a high degree of accuracy, to determine not merely temporary and permanent hardness, but the actual quantities of lime, magnesia, iron, carbonic and sulphuric acids, and chlorine contained in a water, and with this information, the effect of the water on any chemical reaction may in most cases be completely foretold, while the labour involved is much less than that of a complete gravimetric analysis. It must, however, be pointed out that a water with "total hardness" equal to 50 parts of calcium

carbonate per 100,000 is a very hard one, but looked at as a volumetric solution it is only centinormal, and must be determined with an accuracy which should reach $1/50$ th of its strength, and to do this successfully involves many precautions which are quite unnecessary in the use of ordinary normal solutions.

Temporary Hardness.—The credit of having first introduced a practical and scientific method of hardness determination belongs to *Hehner*, who titrates the temporary or bicarbonate hardness with $N/10$ HCl , using methyl orange as an indicator, which is practically insensitive to carbonic acid. The method gives very exact results if certain precautions are taken. Methyl orange is the sodium salt of a colour acid of moderate strength, and the change from the yellow salt condition to the red colour of the free acid * marks the end point, which is sharp and exact when working with strong mineral acids, and with normal solutions. Even in this case it is desirable to use the smallest possible amount of the indicator, but, in working with $N/10$ solutions, the amount of acid required to completely decompose the colour salt becomes very perceptible, and the change from yellow to red is not instantaneous, but passes through orange to pink with the consumption of an appreciable amount of acid. Thus it was found that, using a 10 gm. per liter solution of the indicator in 25 c.c. of water freed from carbonic acid by previous boiling, the following quantities of $N/10$ HCl were required to produce a clear pink: 8 drops of methyl orange solution = 1.5 c.c.; 4 drops = 0.8 c.c.; 2 drops = 0.5 c.c. As even 0.5 c.c. in titrating 100 c.c. of water would correspond to 2.5 parts of hardness per 100,000 and there is always a question as to what particular colour corresponds to the neutral point, the following procedure may be recommended. To 100 c.c. of distilled water, one drop or some other definite quantity of the indicator is added, and titrated, with $N/10$ HCl or H_2SO_4 , to orange, or to the tint to the change of which the eye of the individual operator is most sensitive. The water of which the hardness is to be determined is similarly titrated with the same quantity of indicator, and in a similar beaker, until it exactly matches the distilled water, and from the amount of acid so used the quantity is deducted as a

* A recent view is that the colour substance acts as an acid in presence of bases, and a base in presence of strong acids; but this point is only of theoretical importance.

correction which was required to produce the same colour change with distilled water only. The results so obtained accurately correspond with those got by using alizarin as an indicator in boiling solution, though in the latter method the end reaction is sharper. It may be noted that methyl orange is not absolutely unaffected by carbonic acid, a somewhat crocus-yellow being attained instead of the lemon-yellow reached with pure boiled water, but the difference is insufficient to interfere with its satisfactory use as an indicator.

Each c.c. of acid used per 100 c.c. of water represents 5 parts of CaCO_3 , or 2.8 parts CaO, 2 parts Ca, and 3 parts combined CO_2 per 100,000. Hardness is often expressed in "degrees." French degrees are parts of CaCO_3 , German of CaO, in 100,000, while English were formerly grains of CaCO_3 per gallon (70,000 grs.). It is best, therefore, to avoid the use of the term and state simply as parts CaCO_3 per 100,000.

In place of methyl orange, alizarin paste may be used, with the precautions detailed in the following paragraph.

Permanent Hardness.—Hehner's method for the determination of permanent hardness is less satisfactory than that of temporary. It consists in evaporating 100 c.c. of the water to dryness with a known excess, say 20 c.c., of N/10 sodium carbonate solution, taking up the soluble matter with cold distilled water, filtering off the precipitated calcium carbonate and magnesia on a small filter, washing the precipitate with cold water and titrating back the excess of sodium carbonate in the filtrate with methyl orange or rosolic acid as indicator. With lime-hardness only, and with the precautions above described, the method may be pronounced fairly satisfactory; with magnesia, it is well not merely to evaporate to dryness but to slightly heat the residue to thoroughly decompose any magnesium carbonate present, and even then, the washing should not be excessive, as calcium carbonate is soluble to the extent of 3 parts per 100,000, and magnesia to about 2.5 parts. A more accurate, as well as a more rapid method is to employ a fair excess of sodium carbonate, and to make up the solution to a known volume, say 100 c.c., and pipette off an aliquot part for titration, as the presence of excess of sodium carbonate materially reduces the solubility both of calcium and magnesium carbonates. Both these methods, however, should be superseded, where really accurate work is re-

- quired, by those introduced by Pfeifer and Wartha.* That for the determination of temporary hardness is identical with that of Hehner, except that, in place of methyl orange, a drop of a mixture of about 1 grm. of the purest alizarin paste in 200 c.c. of distilled water is employed. This indicator is surprisingly sensitive; even more so than phenolphthalein, but as it is unfortunately affected by carbon dioxide it is necessary to complete the titration at a boiling temperature. The change is from violet in alkaline solution (perhaps slightly varying in shade with the nature of the particular base present) to a perfectly clear pale lemon-yellow when neutral or acid. The titration of the water should be done with N/10 HCl or H_2SO_4 in a silver, platinum, or hard porcelain basin. The acid should be added in the cold till the violet shade gives place to a clear yellow, and the liquid then brought to a boil, when, with the escape of carbonic acid, the violet colour will return, and should at once be destroyed by the addition of another drop of the acid, and so on, until no further change of colour takes place. It is undesirable to boil the indicator long, especially in an alkaline condition, as a violet deposit is formed on the sides of the basin, presumably of calcium and magnesium alizarates, which can only be dissolved by excess of acid, and is thus apt to cause perceptible errors. In place of titrating to exact neutrality, the acid may be added in very small excess, and the whole of the liberated carbon dioxide boiled off at once, and the solution then brought back to neutrality by N/10 NaOH, the solution boiled for a moment, and the titration completed.

- The results in either case are exact, a fraction of a drop of alkali changing the clear lemon-colour to a dirty yellow. If 100 c.c. of water are used, multiplication of the c.c. of acid by 5, gives the temporary hardness in parts of $CaCO_3$ per 100,000. The boiling must in on case take place in an ordinary glass beaker or flask, as an amount of alkali is dissolved which may lead to serious inaccuracy. Even hard Jena glass is not free from this effect, though the amount dissolved is so small that for most practical purposes it may be neglected. The following experiment will illustrate the point. 100 c.c. of distilled water

* Zeits. angew. Chem., 1902, 198. Prof. Lunge states, in a private letter, that the use of alizarin for this purpose was originated in the laboratory of the Zürich Polytechnicum by Weithi.

boiled for an hour (with additions to maintain the volume) in a Berlin porcelain basin, showed no alkalinity or colour-change with alizarin; in a Jena flask a perceptible change of colour was visible, but pure yellow was restored with one drop of $N/10$ acid, while when boiled in an ordinary Bohemian flask, 0.4 c.c. of acid was consumed, and if the neutralised liquid were boiled further, it again became alkaline, and further additions of acid were required, so that no coincident results could be obtained. With the precautions named, the results with a known solution of hydric calcic carbonate, containing only 5.5 parts of temporary hardness, and whether titrated alone or with additions of magnesium sulphate, were accurate within one part in $100,000$, and experiments with other quantities were equally satisfactory. The manipulation is, however, considerably more difficult than in Hehner's method with methyl orange, so that for temporary hardness the latter is usually preferable.

In the determination of permanent hardness, Pfeifer and Wartha, in addition to the use of alizarin as indicator, have introduced the important improvement of replacing the sodium carbonate of Hehner's method by a mixture of equal parts of $N/10$ sodium carbonate and hydroxide solutions. While, as has been already explained, sodium carbonate perfectly precipitates calcium salts as carbonates on merely boiling, it becomes necessary to evaporate to dryness and to heat whenever any magnesium salt is present, in order to convert magnesium carbonate into oxide, since magnesium carbonate is not sufficiently insoluble. In presence of sodium hydroxide, however, the magnesium carbonate is at once converted into magnesium hydroxide, and perfectly efficient precipitation is obtained by merely boiling for some time with sufficient excess of the reagent. A good excess, say 50 per cent. or more, is essential, not only because it is impossible to say before analysis what proportion of sodium carbonate and what of caustic will be required, but because the presence of the CO_3 ions of the sodium carbonate in the solution greatly lessens the solubility of the calcium carbonate, and similarly the OH ions of the sodium hydroxide lessen that of the magnesium hydroxide. Unless the water is extremely hard, 50 c.c. of the $N/10$ mixed solution to 200 c.c. of water is a convenient and sufficient quantity. The mixture may be boiled until reduced within 200 c.c. in a platinum or porcelain basin, or

more conveniently, and with no material loss of accuracy, in a 300 c.c. Jena flask, but on no account in ordinary Bohemian glass. Even the Jena flask will become perceptibly etched at the water line if used repeatedly. The solution after cooling, is made up to 200 c.c. with distilled water in a gauged flask, and allowed to stand till the precipitated bases have settled, and 100 c.c. is pipetted or siphoned off and titrated. As the quantity named corresponds to 100 c.c. of the original water, and 25 c.c. of $N/10$ alkali, the difference between the acid actually used and 25 c.c. will correspond to the amount of alkali neutralised by the acids of the permanent hardness, and multiplied by 5 will give the latter in terms of milligrammes per 100,000 calculated as calcium carbonate. The temporary hardness will also be precipitated; but, containing no fixed acids, will not interfere. Methyl orange may be used with advantage in place of alizarin, where the extremest accuracy is not required, but the precautions mentioned on p. 17 must be rigorously observed, and the standard solutions must be adjusted with the same indicator as is subsequently used in titration. In place of allowing the precipitate to settle, the solution may be filtered through a small filter, which is carefully washed with the solution, of which the first 50 c.c. or so is rejected, as filters are rarely absolutely free from acidity or alkalinity, and even if at first perfectly neutral, easily absorb acids or ammonia from the laboratory air, unless very carefully protected. Many irregularities occurred in the determinations until this source of error was detected. 15 cm. filters of three different makes were macerated with distilled hot water, and proved in all cases alkaline to methyl orange and acid to phenolphthalein, the difference between the two indicators, + or -, amounting in each case to about 0.75 c.c. of $N/10$ solution.

Alkaline Carbonates.—It occasionally happens that in the determination of permanent hardness, a larger quantity of acid is required to neutralise the mixture than corresponds to the volume of $N/10$ alkali which has been added, and that therefore the permanent hardness would appear as a minus quantity. This somewhat puzzling result is due to the presence of sodium carbonate in the original water, which in this case can have no permanent hardness other than that due to the solubility of calcium carbonate, which cannot be removed by softening.

Where sodium carbonate is thus found, a proportionate amount must be deducted from the temporary hardness, each part of hardness corresponding to 1.06 part of sodium carbonate, and, each c.c. of N/10 acid to 5.3 mgr. of Na_2CO_3 .

Determination of Magnesia.—Since in the ordinary methods of water softening, lime is precipitated as carbonate, but magnesia as oxide, with the consumption of a double quantity of caustic lime or caustic alkali, it is impossible from hardness-determinations alone to calculate the materials required for softening, or the actual weights of the bases titrated, so long as it is uncertain whether or in what proportion magnesia is present. Pfeifer determines this in the following manner. 100 c.c. of the water is neutralised with N/10 acid in presence of alizarin, in boiling solution, exactly as in the determination of temporary hardness, which may precede that of magnesia. A known quantity of clear limewater (25 or 50 c.c.) which should be at least 50 per cent. in excess of that required for precipitating the magnesia present, is measured into a 200 c.c. flask, the hot neutralised solution is rinsed in with boiling distilled water free from carbonic acid, and made up with the latter to 5 c.c. above the mark to allow of contraction in cooling; the flask is tightly corked or stoppered, and well shaken to mix (for which purpose the neck above the mark must be a long one), and set aside to cool and settle. Though not essential, it probably increases the completeness of the precipitation if the corked flask is heated for half an hour or so on the water-bath. I prefer to allow sufficient time for the liquid to completely clear, and to siphon or pipette off 100 c.c. to titrate back with N/10 acid, which may be done cold with phenolphthalein, or hot with alizarin with equal accuracy. If a pipette is used it should be sucked with a rubber tube which can be pinched with the fingers, and the slight excess discharged into another vessel to avoid disturbance of the precipitate, while care is needed to avoid carbonation by the breath. Pfeifer filters, but in this case the strength of the limewater must be determined by a blank experiment conducted in exactly the same way with distilled water; and it is better to reject the first 50 c.c. in each case to avoid error from want of neutrality of the filter-paper, and great care must be taken to filter rapidly, and to avoid possibilities of carbonation by the atmosphere, for which

purpose a sâction filter with a perforated porcelain disc, covered with a neatly-fitted disc of filter-paper, answers well. If, on the other hand, the liquid is settled and pipetted, the risk of carbonation is so small that an equal quantity of the same limewater may be measured direct and titrated, using the same indicator as has been employed for the water, phenolphthalein in the cold being on the whole preferable. Deducting the N/10 acid required for the mixture of limewater and water from that employed for the limewater alone, and multiplying the difference by 5, gives the hardness due to magnesia in terms of milligrammes of calcium carbonate per 100,000, from which actual Mg may be reckoned by multiplying by 0.24; or MgO multiplying by 0.4. Carefully conducted, the method is extremely exact, its accuracy being quite equal to that of the determination of hardness, and probably superior to that of any gravimetric method for such minute quantities. The theory of the process is that, while calcium hydrate will precipitate magnesia, it has no action on lime salts; and a good excess of lime serves not only to quicken the reaction, but to diminish the solubility of the magnesia. If iron is present it will of course be reckoned with the magnesia, and should be determined colorimetrically with thiocyanate (p. 40), and deducted. It may be assumed that it is present in the ferric state, and that therefore 0.24 of Mg corresponds to 0.3733 of Fe. Aluminium, if present, would behave like iron, any traces of alumina dissolved by lime having no effect (on phenolphthalein at least), but it is rare that more than traces of alumina exist in natural waters, though it would have to be reckoned with in river-waters receiving manufacturing effluents, and its estimation would not be particularly easy. Possibly a colorimetric method with alcoholic extract of logwood or some other mordant dyestuff might be devised where the water was required for dyeing, but it is not likely that it would introduce any material error into water-softening calculations, and it would be removed with the other impurities.

Calculation of Chemicals Required for Softening.—Having determined the magnesia, or, more strictly, the acid with which it and any other bases are combined which are precipitable by lime, it becomes possible to calculate the calcium present in the water, by deducting the magnesia hardness from the total hardness, and calculating the remainder into Ca by multiplica-

tion by 0.4. When the proportion of hardness due to magnesia is known, it is possible to calculate the quantities of lime and sodium carbonate required for softening, since magnesium salts, as has been stated, cannot be satisfactorily removed as carbonates, but must be converted into hydroxides by lime or some other caustic alkali; and this applies to the permanent hardness which is converted into carbonate by sodium carbonate as well as to the bicarbonate reduced to carbonate by lime. Thus each equivalent of magnesia present requires an additional equivalent of lime beyond that required by the corresponding calcium salt. Pfeifer gives a formula for this purpose, calculated for German degrees of hardness, which are reckoned in parts per 100,000 of CaO instead of parts of CaCO_3 , as is customary in France and England. I have, therefore, taken the liberty of transposing it into terms of parts of CaCO_3 per 100,000, and slightly modifying some points where it appears incorrect. *Ht* in the formula signifies temporary, and *Hp* permanent hardness, and *Hm* hardness due to magnesia, whether temporary or permanent. The quantities given are in milligrammes per liter, grammes per cubic meter, or lb. per 100,000 gallons of the water to be treated. For complete softening $5.6 (Ht + Hm)$ lime (CaO) and 10.6 Hp dry sodium carbonate; or 28.6 Hp = soda crystals ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$) are required. If hardness is to be softened by liming alone, the quantity required is $5.6 (Ht + Hm)$. This will remove temporary hardness and permanent hardness due to magnesia, but not that due to lime. Finally, for softening with sodium hydroxide and sodium carbonate only, which is sometimes convenient for small boiler installations, we have $8 (Ht + Hm) = \text{NaOH}$ required; $10.6 (Hp - Ht - Hm) = \text{Na}_2\text{CO}_3$ required. Consequently, if the water has less permanent hardness than the sum of the total and magnesia temporary hardness, it cannot be softened completely in this way without leaving excess of sodium carbonate in the water. In such cases barium hydrate may be used with advantage.

If the quantity of CaO for lime-softening only is required, including that consumed by the free CO_2 , it may be obtained experimentally by treating the unneutralised and unboiled water exactly as has been described for the determination of magnesia, and in this case the lime actually consumed in milligrammes per 100 c.c. of water will represent the lime in lb. required to soften

10,000 gallons. It must not be forgotten, however, that commercial limes are far from pure, and the "available lime" of the sample used should be determined as on p. 54.

Commercial barium hydrate may be employed instead of lime to remove temporary hardness, reacting at the same time with the sulphates which are removed as insoluble barium sulphate. Its price and the poisonous character of barium salts are, however, serious obstacles in many cases to its employment.

Free Carbonic Acid.—Some waters contain large quantities of dissolved free carbon dioxide in addition to the "half combined" present as temporary hardness; and though this is not included in any hardness determination, it, of course, combines with and renders useless an equivalent quantity of the lime added for softening, and must, therefore, be taken into account in reckoning the lime required.

Estimation of Free Carbonic Acid (Archbutt).—N/10 sodic carbonate is added slowly from a burette to 100 c.c. of the water, to which a little phenolphthalein has been added, till a faint permanent pink is produced. Each c.c. of N/10 sodic carbonate corresponds to 2.2 mgr. of CO_2 . The reaction ($\text{Na}_2\text{CO}_3 + \text{CO}_2 + \text{OH}_2 = 2 \text{NaHCO}_3$), is accurate but somewhat slow, sodic carbonate being alkaline to phenolphthalein, while hydric sodic carbonate is neutral.

The sample of water must be taken and preserved in a tightly closed and full bottle, as the carbonic acid readily escapes.

For each c.c. of N/10 sodic carbonate used on 100 c.c. of the water, 0.028 gm. of CaO per liter (or 0.028 lb. per 100 gallons) will be required for softening in addition to that required for the hardness (see p. 38).

Estimation of Chlorine.—100 c.c. of the water is titrated with N/10 silver nitrate with potassic chromate as indicator. Each c.c. of silver nitrate corresponds to 3.55 mgr. of chlorine or 5.85 of sodic chloride.

Decinormal Silver Nitrate is prepared by dissolving 17 gm. of pure recrystallised silver nitrate (one-tenth of a gram-equivalent of AgNO_3) in one liter of distilled water free from organic matter.

The Potassic Chromate Indicator is a saturated solution of neutral chromate free from chlorine in distilled water. Its freedom from Cl is tested by slightly acidifying with nitric acid, and adding

a few drops of silver nitrate solution, when no precipitate should be produced.

A few drops of the chromate solution are added to the water, and then silver solution from the burette till the pure primrose-yellow of the chromate is faintly tinged with brick-red, and remains so after vigorous stirring. This method is applicable to the determination of chlorine in all soluble chlorides. In the case of BaCl_2 the barium must previously be converted into sulphate by addition of sodium sulphate, or it will precipitate the chromic acid as barium chromate.*

The solution in which Cl is determined by this method must in all cases be strictly neutral. Acid solutions are easily neutralised by shaking with excess of calcium carbonate or magnesia (free from chlorides) or a solution of sodium acetate may be added, the acetic acid liberated being under these conditions too feebly ionised to interfere. If, however, large amounts of free acid are present, it is wise first to approximately neutralise with soda solution.

Colorimetric Estimation of Traces of Iron.—Evaporate 100 c.c. of water to dryness in a porcelain basin with one or two drops of dilute sulphuric acid, ignite gently, moisten with nitric acid, and evaporate to dryness on the steam bath. Redissolve in water (with a little nitric acid if necessary), and make up to 25 c.c. Mix 10 c.c. of dilute nitric acid (containing 1 c.c. concentrated, sp. gr. 1.35 to 1.40) with 5 c.c. of a 5 per cent. solution of potassium thiocyanate (sulphocyanide) in a Nessler glass, add as many c.c. of the water-residue solution as will produce a convenient colour for comparison, and make up to 50 c.c. with distilled water. A second glass is made up with distilled water, and the same quantities of nitric acid and thiocyanide to about 40 c.c., and a solution containing 0.01 gm. of ferric iron per liter is added from a burette till, after thoroughly mixing by stirring, the colour matches the first. The two glasses are placed side by side on white tile or paper. The comparison should be repeated several times, conveniently by adding say 1 c.c. more of the water solution and re-matching. The volume of standard solu-

The method is conveniently employed as a check on the accuracy of decinormal hydrochloric acid, and soda or sodium carbonate solutions. 10 c.c. of the acid, exactly neutralised by 10 c.c. of the alkaline solution, should require exactly 10 c.c. of the N/10 silver nitrate to produce the red tinge.

tion divided by (original) volume of water used gives parts of Fe per 100,000. The standard solution may be conveniently made by dissolving 0.496 gm. of pure crystallised ferrous sulphate in a little nitric acid in a flask, heating till no more red fumes are given off, making up to 1 liter with distilled water, and diluting the solution 1 : 10 before use.

Considerable care is required to obtain nitric acid free both from nitric oxide and traces of iron. It is best diluted and distilled in a glass retort, and the pure dilute acid should be kept in a white glass bottle. As, however, the same quantity of nitric acid is used in both glasses, the presence of a *trace* of iron in it does not vitiate the result.

Organic Impurities.—While organic impurities even in traces may be of the greatest importance in potable waters, they are rarely of moment to the tanner, except so far as they are connected with the actual presence of injurious bacteria. The bacteriological examination is of too special a character to be usually attempted in the ordinary tannery laboratory; but if the necessary appliances are available it will be well to make plate-cultures (p. 445) on a gelatine bouillon or gelatine peptone medium, and especially to note any organisms which liquefy the jelly, and which are, therefore, likely to attack hide-substance. Actual pelt may be sterilised by treatment with chloroform or ether vapour, with subsequent free washing with sterilised water, or perhaps better by treatment with 2 per cent. caustic soda solution and subsequent neutralisation with a calculated quantity of HCl, and may then be used to test the effect of cultures of special bacteria. No bacteria or yeasts are known to destroy tannin, though they produce acid fermentations in liquors (p. 433). Such acid-forming bacteria are most likely to grow on wort or glucose gelatines of faintly acid reaction.

While the determination of unorganised organic matter is rarely required in the analysis of tannery waters, it is not unfrequently important in connection with cases of alleged river pollution by tannery effluents. Apart from the colour, smell and putrescibility of the water, it is desirable to note its reaction with iron-salts, since traces of tannin of no practical importance give objectionable colorations with the traces of iron naturally present in many waters. A solution of iron-alum is the most suitable reagent. While the total amount of organic matter is not easily determined, apart from the rough results obtained by ignition of

the total solids, useful comparative figures are given by the amount of oxygen absorbed from a solution of potassium permanganate. Many different methods of making this determination have been proposed, yielding different results according to the concentration of the permanganate, and the temperature and time of its action. The following method of Kubel-Tiemann is one of the best, but to obtain comparable results, the directions given must be strictly adhered to.

Pure distilled water is necessary for making up and diluting the solutions, as ordinary distilled water often reduces permanganate because of the volatile organic matters which it contains. To obtain a suitable water, a few crystals of potassium permanganate, and a little pure caustic soda (preferably made from metallic sodium and freshly fused) are added, and the distillation is carried out in glass apparatus, the first fourth which comes over being rejected.

A solution of potassium permanganate is required yielding 0.1 mgr. of oxygen per c.c., and one of pure oxalic acid consuming the same amount. These are best made by diluting in each case 125 c.c. of accurately decinormal solution to 1 liter, the solutions containing 0.395 grm. permanganate, and 0.7875 grm. of pure oxalic acid respectively.

The determination is carried out as follows: 100 c.c. of the pure distilled water, and 5 c.c. of the purest dilute sulphuric acid (1 : 3) are placed in a flask of about 300 c.c. capacity, and the temperature raised to a boil; 2-3 c.c. of the permanganate solution is now added from a glass-tapped burette, the solution is boiled for ten minutes, and 10 c.c. of the oxalic acid is added and well shaken, and the titration with permanganate continued till a faint but permanent pink can be seen on holding the flask over white paper. Very approximately 10 c.c. of the permanganate should be required.

An exactly similar determination is now made, using 100 c.c. of the water to be tested in place of the distilled water. The additional amount of permanganate consumed represents that employed in oxidising the impurities of the water, and each c.c. represents 0.1 part of oxygen consumed per 100,000, or 1 mgr. per liter. If the solutions of permanganate and oxalic acid did not accurately correspond when tested with distilled water, the value obtained must be multiplied by the permanganate required

for 10 c.c. of oxalic acid, and divided by 10. If more than 6-7 c.c. of permanganate are required to oxidise the impurities of the water tested, a less quantity than 100 c.c. must be taken, and the volume made up with distilled water, the result being, of course, multiplied by 100, and divided by the quantity taken. The presence of ferrous iron or nitrites, or great quantities of ammonium salts in the water may introduce errors, but a very short exposure to the air suffices to oxidise and precipitate iron present as ferrous carbonate, and the other impurities will rarely seriously interfere.

More important from the sanitary standpoint than contamination with tan-liquors, is that from old lime-liquors, puers, bates, and drenches containing putrescible organic matter. In rivers containing fish, the presence of caustic lime is also specially objectionable, and is easily tested for with phenolphthalein, and if necessary estimated by titration. Calcium carbonate, which does not redden phenolphthalein, is practically harmless, soon settling as mud.

Nitrogenous matter is generally estimated by the ammonia which it will yield, and medical officers of health are very fond of the old "albuminoid ammonia" test, from its apparent ease of execution. However useful this may be as a first test for nitrogenous impurity in potable waters, it is totally illusory and unreliable for ordinary factory effluents, from the very small quantity of water which can be used and the consequent multiplication of errors, as well as from the great variations arising from small differences in manipulation. A much more reliable method, in these cases, is that of Kjeldahl as modified for the purpose by Brown and Martin and others. For the outlines of this method, see p. 64.

Complete Gravimetric Analysis.—The volumetric methods already given are so accurate, if carefully carried out, that it is rarely necessary for the purposes of the tanner, to resort to gravimetric analysis, but occasionally reasons arise which make it necessary to know all the mineral constituents and their quantity, and the following details are therefore given. For the general methods of manipulations required, Section I. must be consulted; but unless considerable chemical experience has been gained, the fuller accounts of the regular analytical works should be studied.

The water, if turbid, must be well shaken before samples are drawn for any determinations, and 500 c.c. or 1 liter measured into a flask, and then filtered through a dried and tared quantitative filter paper (p. 13). The filter is washed with a little distilled water, which is added to the filtrate, and is then dried in the water oven (or air oven at 105° – 110° C.) till constant, and weighed: the gain of weight is "mud and suspended matter." The filter is now ignited, and the residue weighed and entered as "inorganic suspended matter," and the difference from the weight of residue at 100° C. as "organic suspended matter." This is not strictly accurate, as some part of the loss may be due to combined water.

The filtrate, or 500 to 1000 c.c. of the original water, if quite clear, is now evaporated to small bulk in a weighed platinum (or porcelain) basin over a small flame applied at one side of the basin to avoid spurting, the water being added in small quantities as it evaporates. When reduced to perhaps 50 c.c. the basin is placed on the steam bath and evaporated to dryness, and then dried at 100° to 110° C. till constant, cooled and weighed. The weight of the residue is "total solids." It is gently ignited and the loss entered as "organic matter and combined water," and the residue as "inorganic constituents." If the ignition has been at all strong, it is best to moisten with solution of ammonium carbonate to restore CO_2 , and again ignite very gently. Magnesium chloride loses its Cl on ignition.

The residue is moistened with concentrated hydrochloric acid, and evaporated to dryness on the steam bath, and, after drying at 120° C. for two hours to render silica insoluble, is taken up with distilled water, more hydrochloric acid being used if any dark-coloured residue (ferric oxide) remains undissolved. The solution is filtered, and the residue, after thorough washing, is ignited and weighed as *silica*, SiO_2 . It should be colourless, and on boiling with dilute hydrochloric acid the solution should give no precipitate with ammonia and ammonium oxalate (calcium sulphate).^{*} The filtrate is boiled with a little nitric acid to oxidise ferrous salts, and ammonia is added till the solution smells pretty strongly, and the boiling continued a short time. If a precipitate (ferric hydrate, alumina, phosphates) is formed,

^{*} If any precipitate of calcium oxalate is obtained, it must be estimated and added to that found in the ordinary course of analysis.

it is filtered off and washed and ignited and weighed as *ferric oxide*, Fe_2O_3 , from which Fe may be calculated as 112 : 160, or by multiplication by 0.7. If the precipitate is considerable it is well to wash by decantation, re-dissolve in a little HCl, and precipitate again with ammonia, as otherwise lime and magnesia are apt to be carried down with the iron. It will contain any alumina or phosphates present, for the separation of which chemical text-books must be consulted, but the whole precipitate is usually so small in quantity as to render this negligible. (Cp. also p. 365.) To the filtrate (or clear solution) ammonium chloride is added if little hydrochloric acid has been used, and then excess of ammonium carbonate and a little ammonium oxalate, and the solution is boiled, and, if possible, set aside for twelve hours in a warm place. It is then filtered, and the precipitate, after washing, is strongly ignited, first over the Bunsen burner, and then before the blow-pipe till the weight remains constant. It is weighed as *lime*, CaO , from which Ca may be calculated as 40 : 56. If the quantity is large, it is better to ignite very gently and weigh as *calcium carbonate*, CaCO_3 . It should then be moistened with ammonium carbonate, dried in the water oven, and again very gently ignited, when no gain of weight will take place unless the first ignition has been too strong. The atomic weights are : $\text{Ca} = 40$, $\text{CaO} = 56$, $\text{CaCO}_3 = 100$.

The filtrate contains salts of Mg and the alkalis from the water, and ammoniacal salts which have been added. The Mg may be very accurately determined by the volumetric method with lime water, given on p. 36. To determine directly, the filtrate is evaporated to small bulk, strongly acidified with nitric acid and evaporated to dryness in a porcelain basin under an inverted funnel to destroy excess of ammonium chloride, or the evaporation may be carried to dryness and the ammonium chloride expelled by simple heating till no further fumes are given off. The funnel and basin are rinsed with distilled water into a beaker, excess of ammonia and sodium phosphate and a little ammonium chloride added, and the solution covered up and allowed to remain undisturbed for 12 to 24 hours. The crystalline precipitate is collected on a filter and washed with a mixture of 1 part strong ammonia to 5 parts water, dried and detached as completely as possible from the filter, and transferred to a crucible, which is

heated at first gently with the cover on, and then ignited. The filter is burnt separately, rolled in platinum wire, and the ash (free from carbon) is added to the precipitate and strongly ignited for 15 minutes. The residue is magnesium pyrophosphate, $\text{Mg}_2\text{P}_2\text{O}_7 = 222$, from which $\text{Mg}_2 = 48$ is calculated.

The alkalis are most conveniently determined in the filtrate from the sulphuric acid determination (see below).

Determination of Sulphuric Acid.—At least 250 c.c. of the original water is rendered distinctly acid with hydrochloric acid, and is concentrated by evaporation to about 100 c.c.; and to the boiling liquid excess of barium chloride solution is added (5 to 10 c.c. of a 10 per cent. solution). The mixture is allowed to stand for some hours in a warm place, and the clear liquid is poured through a quantitative filter, and the precipitate washed several times with hot water by decantation, the wash-waters being poured through the filter, into which the precipitate is finally transferred and well washed, dried, ignited and weighed. It consists of *barium sulphate*, $\text{BaSO}_4 = 233$, from which the $\text{SO}_4 = 96$ is calculated.

In place of gravimetric estimation with BaCl_2 , sulphuric acid, free or as alkaline sulphates, may be conveniently and accurately estimated by precipitation as benzidine sulphate according to the elegant method of Wolf Müller* or its modification by Raschig.† For the estimation of sulphates in water and for many other technical purposes, Wolf Müller's method is perfectly satisfactory, and will be here described, but in presence of ferric salts and some other substances fails to give satisfactory results; and to overcome these special difficulties Raschig's method has been devised, for details of which the original papers must be consulted.

Wolf Müller's method depends on the fact that while sulphuric acid, either free or as sulphate, is very completely precipitated by benzidine chloride, the base benzidine is so weak that any strong acid in combination with it can be completely estimated by titration with NaOH and phenolphthalein, as if free. If, then, an excess of an acid solution of benzidine chloride, of which the acidity as compared to $\text{N}/10$ NaOH is exactly known, is run into a solution of an alkaline sulphate carefully neutralised to phenolphthalein, the sulphuric acid combines with the benzidine

* Chem. Berichte, 1902, p. 1587.

† Zeit. angew. Ch., 1903, Hefte 26, 34; Collegium, 1904, p. 170 *et seq.*

and is precipitated and filtered off, while an equivalent portion of the hydrochloric acid is neutralised by the base, and on titrating back with NaOH, this deficiency is determined and calculated as SO_4 .

For the practical execution of the method, 1 grm. of commercial benzidine base is rubbed up with a little water and dissolved as completely as possible by warming in 100 c.c. of N/1 HCl, made up to 1 liter and filtered. Such a solution will be approximately N/10 as regards acid, and about 30 c.c. will precipitate 0.1 grm. H_2SO_4 , leaving sufficient excess of benzidine in solution. It is desirable that the requisite quantity of the benzidine solution should be measured, and the sulphate solution added to it, so that the benzidine is always in excess, and after well mixing, allowed to stand at least five minutes, while for very dilute solutions, or those containing traces of organic matter, some hours are not too much, and where much organic matter is present, precipitation is frequently imperfect. In the estimation of the sulphates in waters, it will usually be sufficient to add 200 c.c. of the water to 50 c.c. of the solution, and after filtration to twice titrate 100 c.c. corresponding to 20 c.c. of benzidine solution and 80 c.c. of the water. If 20 c.c. of the benzidine solution requires 19.3 c.c. of N/10 soda, and 100 c.c. of the filtrate 6.7 c.c., we have
$$\frac{(19.3 - 6.7) \times 0.0048 \times 100}{80} = 0.0726 \text{ grm. } \text{SO}_4 \text{ per}$$

100 c.c. or 72.6 parts per 100,000. The water must have been previously boiled to expel CO_2 and remove temporary hardness, or an amount corresponding to the temporary hardness of the water must be added to the number of c.c. of soda required for neutralising the filtrate, and in any case it is well to raise the liquid to a boil to expel CO_2 before completing the titration, if the greatest accuracy is required.

In applying the method to sulphates of bases which do not redden phenolphthalein, it is necessary to convert them into alkaline sulphates by treatment with sodium carbonate, and subsequent neutralisation and boiling to expel CO_2 , or to adopt Dr. Raschig's modification (*loc. cit.*) in which the benzidine sulphate is filtered off, washed and titrated. In all cases of doubt the absence of sulphates in the filtrate should be ascertained by testing with barium chloride, which at most should show a faint turbidity after a considerable time.

Benzidine is $\left\{ \begin{smallmatrix} \text{C}_6\text{H}_4\text{NH}_2 \\ \text{C}_6\text{H}_4\text{NH}_2 \end{smallmatrix} \right\}$. It has a molecular weight of 184, and, being a di-amido compound, combines with 1 molecule of sulphuric or 2 of hydrochloric acid.

Determination of Alkalies.—Boil the filtrate from barium sulphate, p. 46, with excess of baryta water or pure milk of lime to remove magnesia, iron and phosphoric acid. Filter, concentrate filtrate, add ammonia, ammonium carbonate and a few drops of ammonium oxalate, evaporate to dryness, ignite very gently, and wash residue with distilled water, filter, and evaporate filtrate to dryness in a weighed basin with a few drops of hydrochloric acid. It is safer to repeat the treatment with ammonium carbonate and oxalate, as traces of lime or baryta are very liable to escape precipitation. The residue is alkaline chlorides. If potassium is present in appreciable quantities, which is very rarely the case, it may be determined as chloroplatinate, or the chlorine may be determined (p. 39) and calculated as sodium chloride, which is deducted from the actual weight of mixed chlorides. The remainder multiplied by $\frac{74.6}{39.1 - 23}$ or 0.463 represents the potassium chloride.

Statement of Results.—As chemical analysis furnishes no direct information as to the state of combination in which the acids and bases found existed in the original water, it is customary in the first instance to state them separately, the acids usually being calculated as radicals (ions) which with the base form the salt, thus $\text{Ca} + \text{SO}_4$, $\text{Ca} + \text{CO}_3$, etc. Afterwards from these figures the salts existing in the water may be arranged with acids and bases in combining proportion and usually on the assumption that CO_2 first combines with Ca and then with Mg, then SO_4 in the same order. The CO_3 is calculated from the temporary hardness, each part of hardness corresponding to 0.6 part of CO_3 .

Probably this will be best illustrated by the calculation of an imaginary somewhat hard water, of temporary hardness 16.0 and permanent 20.8, and total inorganic solids (p. 44): 46.5 parts per 100,000, and of the composition shown in table on next page.

Of course it often happens in practical work that the figures do not fit quite so exactly as in the above, but at least the total inorganic solids should very approximately equal the sum of

the individual determinations stated as above. The method furnishes a useful check on analytical work, but is otherwise of little practical value, as the original figures together with the hardness

	Per 100,000.	CaCO ₃ .	CaSO ₄ .	MgSO ₄ .	NaCl.	SiO ₂ .
Ca	8.9	6.4	2.5
Mg	3.5	3.5
Na	1.2	1.2	..
CO ₂	9.6	9.6
SO ₄	20.0	..	6.0	14.0
Cl	1.9	1.9	..
SiO ₄	1.4	1.4
Total	46.5	16.0	8.5	17.5	3.1	1.4

determinations furnish all the information required by the chemist, and we have no real knowledge as to the combinations actually existing in water, and according to modern theory the statement as uncombined ions probably more nearly represents the actual facts than any arrangement in definite salts.

In judging of the suitability of a water for tanning, it may be generally stated that, in absence of serious organic impurity, the softer it is the better. The amount of temporary hardness is of the first importance, as, when employed for washing goods after unhairing, it fixes both the lime in the hide and that present as temporary hardness in the form of carbonate, roughening the grain and causing stains and discoloration in the liquors. The lime thus fixed is not removed by puering or in the ordinary course of bating, nor even by drenching, unless the drench is more than usually acid. Temporary-hard waters are also very objectionable for dissolving extracts and extracting tanning materials, as, in absence of stronger acids, the lime carbonate reacts with the tannins, of which it neutralises and renders useless many times its own weight, forming lime tannates which oxidise with the formation of dark-coloured compounds in the liquors.

Permanent hardness is much less injurious in this respect, as the tannins cannot displace the stronger acids directly, but will react in presence of alkaline salts of weak acids, which always exist in tanning liquors, the tannin combining with the lime of

the sulphate or chloride, while the sulphuric or hydrochloric acid combines with the alkali, displacing the weak organic acid ; but of course this can only take place in nearly neutral liquors, and may be prevented by the addition of a calculated quantity of acetic, formic or lactic acids sufficient to decompose the lime salts formed. It is possible also that permanent hardness diminishes the solvent power of the water for the more difficultly soluble tannins.

Considerable experimental work has been done on this subject by Nihoul,* and by Paessler and Appelius,† who have arrived at almost opposite conclusions as to its importance ; though both agree that temporary hardness causes some loss, and decided darkening in colour, both of the liquor and the leather tanned with it. The explanation of these differences in result is probably to be sought in the different amounts of acidity, especially including free carbonic acid present, and in the temperatures of extraction ; the injurious effect being most serious when heat was employed, and being especially marked with sumach.

In the manufacture of the finer leathers, hardness is injurious in several ways beside those already mentioned. In leather-dyeing, temporary hardness causes precipitation of the basic coal-tar colours, which however can be prevented by the addition of small quantities of acetic acid. Neither temporary nor permanent hardness interfere with the ordinary use of acid colours, as acid is usually added in considerable excess (see p. 376), and with the dye-woods they are rather advantageous than otherwise.

In fat-liquoring of chrome and other tannages the influence of hard water of either sort is very marked, causing the curdling and separation of the fat-liquors, with the formation of insoluble lime and magnesia soaps ; and in scouring with soaps it is equally objectionable. Theoretically each part of hardness per 100,000 destroys about 12 parts of soap (sodium stearate or oleate), but really the loss is greater, though somewhat variable. For this reason, where destruction of soap is the important factor,

L'influence de la nature de l'eau sur l'extraction des matières tannantes.
Collegium, 1902, i. 80.

† *Einfluss der Härte des Wassers auf die Ausnutzung der Gerbmaterien.*
Collegium, 1902, i. 223.

the individual determinations stated as above. The method furnishes a useful check on analytical work, but is otherwise of little practical value, as the original figures together with the hardness

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Ca	8.9	6.4	2.5
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Na	1.2	1.2	..
CO ₂	9.6	9.6
SO ₄	20.0	..	6.0	14.0
Cl	1.9	1.9	..
SiO ₄	1.4	1.4
Total	46.5	16.0	8.5	17.5	3.1	1.4

determinations furnish all the information required by the chemist, and we have no real knowledge as to the combinations actually existing in water, and according to modern theory the statement as uncombined ions probably more nearly represents the actual facts than any arrangement in definite salts.

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Permanent hardness is much less injurious in this respect, as the tannins cannot displace the stronger acids directly, but will react in presence of alkaline salts of weak acids, which always exist in tanning liquors, the tannin combining with the lime of

but in water used for liming it increases the plumping, and makes the unhairing more rapid on account of the caustic soda formed. Free carbonic acid also fixes the lime in the grain of limy goods, but is not otherwise injurious.

Iron, even in traces, is to be avoided; a quantity so small as one part in a million has been shown under some circumstances to produce appreciable discoloration both of liquor and the leather tanned in it, though it is generally present in larger quantities than this in ordinary tanning liquors.

The following analyses of actual waters will give some idea of the variations which may be expected:—

TECHNICAL EXAMINATION OF WATERS FROM VARIOUS SOURCES.
(Parts per 100,000.)

Source.	Temp. Hardness.	Perm. Hardness.	Chlorine.	Nag CO ₃ .	Total Solids.	Loss on Ignition.
1. Gomshall, river water ..	6·8	1·0	1·8	nil
2. „ shallow well ..	16·5	7·0	2·1	„
3. „ artesian well ..	6·5	2·5	1·6	„
4. North Shields, surface ..	37·5	49·0	38·0	„
5. Newcastle, town supply ..	19·0	5·4	1·6	„	24·8	..
6. Well near Hexham	4·3	3·0	1·3	„
7. Stourport, A.	27·8	19·5	15·3	„	100·0	..
8. „ B.	8·0	1·0	1·4	„
9. Leeds, Kirkstall Road ..	28·2	14·4	3·9	„	66·4	..
10. „ Meanwood Road ..	6·5	nil	2·8	39·9	66·3	11·8
11. „ deep well	4·0	39·0	5·1	nil	65·9	20·6
*12. Chesterfield, A.	7·5	5·6	1·4	„	19·6	4·5
13. „ B. (probable sewage contamination)	15·0	25·3	12·3	„	64·8	..
14. London district	25·0	nil	5·0	9·0
*15. „	25·0	9·0	1·7	nil	36·0	1·3
*16. „	30·8	88·5	63·8	„	627·8	..
*17. „ Guy's Hosp.	6·0	2·0	13·9	„	73·8	1·3
*18. „ Cawnpore	9·4	nil	1·3	10·6	145·7	3·9
*19. Limerick	3·5	13·0	2·0	nil	22·7	0·7
*20. Stourbridge	18·0	24·5	13·7	„	49·6	8·2
*21. „	20·0	32·5	16·2	„	97·3	22·5
22. Leicester	26·5	10·8	2·8	„	53·0	20·9

DETAILED ANALYSIS OF SOME OF ABOVE WATERS. (Marked *.)

	Al.	Ca.	Mg.	Fe.	Na.	SO ₄ .	CO ₃ .	Cl.	SiO ₂ .	CO ₂ Free.
12. Chesterfield	3'1	1'1	6'1	4'5	1'4	..	0'8
15. London district	6'3	4'3	trace	..	6'0	15'0	1'7
16. " "	13'7	60'4	..	1'1	41'3	70'3	20'5	63'9	330'5	..
17. " "	1'5	1'0	..	23'7	15'8	13'4	13'9	1'1	..
18. Cawnpore	1'8	0'3	0'2	4'6	4'1	11'6	1'3	1'0	..
19. Limerick	3'1	2'1	2'2	..	9'0	2'1	2'0
20. Stourbridge	10'9	1'0	0'2	1'9	7'6	11'4	6'2	1'3	2'6
21. " "	16'5	1'4	1'1	6'0	15'2	12'3	13'7	0'9	4'4

SECTION IV.

DEPILITANTS.

Solubility of Limes.—The strength of lime-water given by different limes is found to vary slightly.

The explanation of these results is not very easy, but probably depends on the presence of some other soluble base in addition to the lime. It harmonises with the old belief of tanners that pure chalk lime is milder in its action on skin than that made from less pure limestones. The solubility of any given lime is easily determined by adding it in excess to water in a stoppered flask, and shaking frequently till a solution of constant strength is obtained, of which a measured quantity is titrated with N/10 hydrochloric acid and phenolphthalein. Saturated lime water may be conveniently used as an alkaline standard solution for many purposes, and if kept on excess of lime, is always caustic, and varies little in strength at ordinary laboratory temperatures. It is better to allow it to settle and to remove the clear solution with a siphon or pipette than to filter, which often reduces the strength. The solution is nearly $\frac{1}{20}$ normal, but for accurate work its strength should be occasionally determined with N/10 acid. The solubility of lime diminishes with increasing temperature.

The following table gives the strength of a pure saturated lime solution for various temperatures as [determined by Mr. A. Guthrie in the author's laboratory.

100 c.c. of saturated lime water at				5° C. contain	0·1350	gram. of CaO.
"	"	"	10	"	0·1342	"
"	"	"	15	"	0·1320	"
"	"	"	20	"	0·1293	"
"	"	"	25	"	0·1254	"
"	"	"	30	"	0·1219	"
"	"	"	35	"	0·1161	"
"	"	"	40	"	0·1119	"
"	"	"	50	"	0·0981	"
"	"	"	60	"	0·0879	"
"	"	"	70	"	0·0781	"
"	"	"	80	"	0·0740	"
"	"	"	90	"	0·0696	"
"	"	"	100	"	0·0597	"

Determination of "Available" Lime.—The practical value of lime for the tanner is easily determined by drawing a sample by breaking off small pieces from a number of lumps of the bulk, coarsely pulverising them in a mortar, and then grinding a portion as fine as possible, and transferring it at once to a stoppered bottle for weighing. A portion of this not exceeding 1 gram. is shaken into a stoppered liter flask, which is filled up with hot and well-boiled distilled water, and allowed to stand for some hours with occasional shaking. When cold it is filled to the mark with recently boiled distilled water, and well shaken again and allowed to settle, or filtered with as little exposure to the air as possible, and 25 or 50 c.c. withdrawn with a pipette and titrated with N/10 hydrochloric or sulphuric acid and phenolphthalein. Each cubic centimeter of N/10 acid equals 0·0028 gram. CaO. The presence of a small quantity of insoluble sediment in the liquid titrated does not affect the phenolphthalein.

Another method, depending on the solubility of lime in cane sugar solutions, is described by Messrs. Stone and Scheuch.† One gram. of finely powdered quicklime is shaken for twenty minutes with 150 c.c. of a 10 per cent. solution of pure lump sugar, and 10 c.c. of the filtered solution titrated as before with phenolphthalein and N/10 hydrochloric acid. Calcium car-

* Journ. Soc. Ch. Ind., 1901, p. 224.

† Journ. Amer. Chem. Soc., xvi, p. 721; Chem. News, 1894, p. 278.

bonate, magnesia, alumina and ferric oxide are not dissolved by sugar solution, and do not interfere. This method gives accurate results with careful manipulation, but in the author's experience it is safer to allow the solution to stand some hours, and it is not on the whole to be preferred to that given above. A solution of lime in cane sugar solution may be used as a standard solution, with phenolphthalein as an indicator where a stronger solution than lime-water is desirable, and the addition of sugar has also been used to shorten the time of liming. A 25 per cent. solution of cane-sugar will dissolve lime to nearly N/1 strength.

If desired, a complete analysis of a lime can be made by gravimetric methods similar to those employed in determining the mineral constituents of water (p. 43), but this is rarely necessary for the purposes of the tanner. The total bases existing as oxides, carbonates and easily decomposable silicates, are readily determined by treating 1 gram. of the finely powdered sample with 50 c.c. of N/1 HCl, and titrating the excess of acid.

Sodium Sulphide, crystallised sulphide of sodium, $\text{Na}_2\text{S} \cdot 9\text{Aq}$, contains 67.5 per cent. of water, and 32.5 per cent. Na_2S . A fused salt is also sold, containing a much larger percentage of Na_2S . It will generally be sufficient to determine the sodium and sulphur, any sodium in excess of that required to form the sulphide being calculated as sodic carbonate, which is gradually formed by exposure to the air.

10 gram. or conveniently 12 gram. of the sample is dissolved in water and made up to 1 liter. Sodium is determined by titrating with N/10 HCl or H_2SO_4 in presence of methyl-orange, which is not sensitive to SH_2 . Each c.c. of N/10 acid is equal to 2.3 mgr. of Na or 3.9 mgr. of Na_2S , or 12 mgr. of the crystallised salt, so that if 12 gram. are weighed out, the solution of the pure salt would be decinormal.

Determination of Sulphur as Sulphide.—14.35 gram. of pure crystallised zinc sulphate ($\text{ZnSO}_4 \cdot 7\text{Aq}$) is dissolved in water, and ammonia is added till the precipitate which is at first formed is dissolved, and the whole is made up to a liter. An alternative method is to dissolve 3.25 gram. of pure zinc in dilute sulphuric or hydrochloric acid with the aid of a piece of platinum foil, add excess of ammonia and make up to 1 liter. The solution is decinormal, and each c.c. equals 1.6 mgr. sulphur, or 12 mgr. of

the crystallised sulphide of sodium. If 12 grm. of the sample is made up to 1 liter, and 100 c.c. titrated, each c.c. of either N/10 solution will correspond to 1 per cent. of pure crystallised salt. The standard solution is added with constant stirring to, say 25 c.c. of the sodium sulphide solution in a beaker, and after each addition a drop is taken from the beaker and placed on a piece of filter paper on a white plate, side by side with one of a solution of lead acetate, but not actually touching it, so that the two run together by capillarity. (A somewhat more delicate lead indicator may be made by dissolving lead acetate in solution of sodium tartrate, or tartaric acid made strongly alkaline with sodium hydrate and filtering.) So long as any unprecipitated sulphide is present, a black or brown ring is formed where the two liquids come in contact. Care must be taken that the lead solution does not reach the precipitated zinc sulphide, which is always blackened by it. It is best first to make a rough determination, adding, say, 2 c.c. of standard solution at a time; and having in this way determined the approximate quantity required, nearly the full amount may be added at once. A solution of sodium sulphide may similarly be employed for the determination of zinc.

Instead of using a lead salt as indicator, a solution of sodium nitro-prusside may be employed, drops of which are simply spotted on a white tile and give a strong purple reaction with the least trace of alkaline sulphide.

The zinc process may be employed for the determination of sulphur in other alkaline sulphides, but where polysulphides are present a yellow zinc sulphide is formed, probably a polysulphide, and the lead indicator gives an orange instead of a black ring. As a consequence the whole of the sulphur is not determined, but only that corresponding to the normal sulphide, and which would be liberated as SH_2 on treatment with an acid. Since it is probable that only this portion of the sulphur is effective in unhairing, this may probably be reckoned as an advantage rather than the reverse.

Sulphides may also be determined by titration with N/10 iodine,* but as many other sulphur compounds also reduce iodine, the method becomes complicated and is not to be recom-

* Jean, *Ann. de Chim.*, ii. (18), p. 341; *Analyst*, 1897, p. 306; *Journ. Soc. Ch. Ind.*, 1897, p. 1041.

mended for the analysis of depilants, though quite suitable for the determination of small quantities of hydrogen sulphide.

• *Realgar, Rusma, Red Arsenic*, an impure form of As_2S_3 , made by fusing suitable proportions of arsenious acid and sulphur, and much used in combination with lime as a depilatory, especially in the manufacture of glove-kid and other light leathers. The realgar is usually mixed with excess of hot slaking lime for this purpose, and the decompositions which occur are not well understood and probably vary with the temperature. It is said that a mixture made with hot lime has a more powerful effect than a mixture made in the cold, or even with boiling water. Probably in all cases calcium sulphhydrate is the active depilant.*

Orpiment or Yellow Arsenic Sulphide, As_2S_3 , is generally said to be unsuitable for depilation, but in the author's experiments it proved more efficient, weight for weight, than realgar, and no difference could be detected in the character of the result. The yellow arsenic is now much cheaper than the red, as it is a by-product in the purification of arsenical sulphuric acid. Both are, of course, very poisonous, and must be handled with great caution, and lime liquors containing them must not be run into rivers; and they do not appear to have any real advantage over calcium sulphhydrate, or the mixture of equivalent quantities of sodium sulphide and calcium chloride, suggested by the author for use where the powerful alkaline swelling action of sodium sulphide used alone as an addition to limes is objectionable.

Analysis of Arsenic Sulphides.—The sample must be very finely pulverised in an agate mortar. Non-volatile impurities are determined by igniting a small quantity, not exceeding 1 gm., in a porcelain crucible over a good Bunsen burner and weighing the residuc. As the fumes are very poisonous, the operation must be performed in a good draught-chamber.

Both sulphides of arsenic are soluble in the cold in caustic soda or potash solutions. 1 gm. of the finely powdered sample is digested for some hours with 50 c.c. of 10 per cent. caustic soda solution with frequent shaking, and made up to 100 c.c. with

* Stiasny (Gerber, 1906, pp. 272, 288), shows that only a small quantity of the arsenic goes into solution, and that the soluble arsenic compounds have no depilatory effect. Eitner (Gerber, 1907, p. 481), found that they also had no effect as antiseptics, and that it was impossible to distinguish skins treated with calcium sulphhydrate only from those on which arsenic was used. Stiasny (loc. cit.) shows that the presence of OH as well as SH ions in solution is essential to satisfactory depilation.

water, and filtered. The filter is well washed, the wash-waters being rejected and not allowed to mix with the filtrate; the filter is ignited, and the impurities are weighed. The sulphide-sulphur may be determined in the filtrate by the zinc method (p. 55), but in a commercial realgar only amounted to about 12 per cent., while the total sulphur theoretically present in pure As_2S_2 is 29.9 per cent. It is probable, however, that the sulphur determined with zinc is proportional to the depilatory power of the sample, and may be safely used for comparison of relative value and for determining residual sulphide in lime liquors.

Both sulphides are liable to contain excess of either As_2O_3 or of sulphur, according to their mode of manufacture, and for the purposes of the tanner As_2O_3 is of no value and free S of very little. Hence the determination of total sulphur or total arsenic is not of much practical importance, except as showing that they are present in the proper proportions. The estimation is best made by oxidising sulphur to sulphuric acid and arsenic to arsenic acid by digestion with nitric acid.

Estimation of Sulphur.—0.10–0.2 gm. of the sample is digested with a mixture of 3 volumes of concentrated nitric acid and 1 volume concentrated hydrochloric acid, and the solution evaporated repeatedly nearly to dryness with addition of concentrated HCl. The solution is diluted and filtered if necessary, and precipitated with excess of BaCl_2 solution and the precipitate washed, dried, ignited and weighed with the usual precautions (p. 12). The weight of the precipitate multiplied by $\frac{32}{233.5}$ or 0.1371 gives that of sulphur present in the quantity taken.

Estimation of Arsenic.—0.1–0.2 gm. of the sample is boiled with concentrated nitric acid till dissolved, diluted with water, rendered strongly alkaline with ammonia, filtered if necessary, and precipitated with magnesia solution (11 gm. cryst. magnesium chloride, 14 gm. ammonium chloride, 70 c.c. strong ammonia and 130 c.c. water) and $\frac{1}{2}$ its volume of strong alcohol. The solution is allowed to stand at least 12 (and preferably 48) hours; the precipitate is filtered off and washed with a mixture of 2 parts strong ammonia, 2 parts water and 1 part alcohol. After drying the filter in an air or water-oven, the precipitate is

transferred as completely as possible from the filter on to glazed paper; the filter is replaced in the funnel and washed with a little hot dilute nitric acid, which is evaporated to dryness in a weighed porcelain crucible; the remainder of the precipitate is added, and the covered crucible is slowly heated, finally to a dull red. The cover is now removed and the open crucible strongly ignited over a powerful flame, placed while still hot in an exsiccator over sulphuric acid, and weighed when cool. The weight of $\text{Mg}_2\text{As}_2\text{O}_7 \times \frac{150}{311}$, or $0.483 = \text{As}$.

A shorter but less exact method is, after oxidation with fuming nitric acid, simply to evaporate the solution to dryness in a weighed porcelain crucible, drive off the sulphuric acid by cautious heating, and finally raise the crucible to dull redness, cool in an exsiccator over P_2O_5 and weigh as As_2O_5 . Any non-volatile impurities will be included in the result. After weighing, the residue should be re-dissolved and tested with BaCl_2 for sulphuric acid—too high a temperature of ignition will cause loss of arsenic.

SECTION V.

THE ESTIMATION OF AMMONIA AND THE DETERMINATION OF NITROGEN.

THE estimation of ammonia is one of the most important of those required by the leather trades chemist, not only because its presence in lime liquors has a very considerable effect on the unhairing process, and indicates to some extent the destruction of hide-substance, but because in the Kjeldahl process all the nitrogen present in organic matters is converted into sulphate of ammonia by digestion with concentrated sulphuric acid, and consequently the estimation of the ammonia so formed is a measure of the quantity of hide-substance which has been treated,

and thus forms a means for its estimation both in solution and in the form of leather.

Some information is given on pp. 26 and 71 with regard to the ordinary testing of ammonia solutions and ammonium salts, but where these occur together with organic matter further precautions are required.

In the case of lime liquors, all the ammonia is free, together with an excess of caustic lime, which, if the solution is heated for any length of time, acts upon the nitrogenous matter present, decomposing it and producing further quantities of ammonia. It is therefore desirable to avoid heating as much as possible, and Schloessing's method has been commonly used. It has, however, the disadvantage of being very slow, and in very weak ammonia solutions it is certain that the whole of the ammonia is not really estimated.

Experiments have been made in the Author's laboratory* to devise a more rapid method of ammonia estimation in the cold by placing the lime liquor in an absorption apparatus connected with a second containing standard acid, and gently sucking a current of (ammonia-free) air through the apparatus so as to carry the ammonia into the acid. Good comparative results were obtained, but it is difficult without the use of heat, absolutely to carry over the whole of the ammonia. With a suitable apparatus and a temperature of about 65° C., however, the estimation is very rapid and exact, and no appreciable evolution of ammonia from the nitrogenous compounds present in a lime liquor occurs, so that where many estimations are required the process is much to be recommended, as once the apparatus is arranged, very little attention is required. The arrangement employed is shown in Fig. 6, the air, previously freed from carbonic acid and ammonia, is passed into a wide test-tube partially filled with broken glass and containing 50 c.c. of the lime liquor, through a tube so arranged as continuously to raise the liquor along with the air and allow it to trickle down over the broken glass, while the air is drawn through an absorption tube containing 30-50 c.c. of N/50 sulphuric acid, or of a stronger standard acid if the quantity of ammonia is excessive. The

* Procter and McCandlish, "The Estimation of Ammonia in used Lime Liquors," *Journ. Soc. Ch. Ind.*, 1906, p. 254; *Colleg.*, 1906, p. 270.

THE ESTIMATION OF AMMONIA.

test tube is surrounded with water at about 90°C ., sufficient to raise the interior of the tube to about 65°C . The detail of the bubbling tube is shown on a larger scale on the left of the figure. A few drops of turpentine may be added to the lime liquor to prevent frothing. With a steady current of air, the operation is complete in thirty minutes. Dr. Nihoul has devised a somewhat similar but continuous apparatus, in which the lime liquor is allowed to trickle in a slow continuous stream over the broken glass, through which the air is aspirated. In this way it is

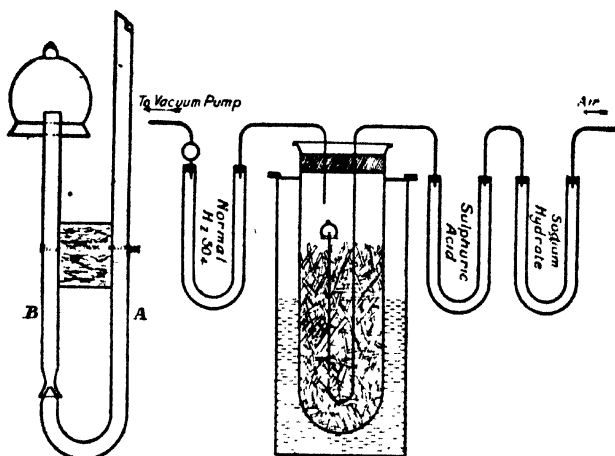


FIG. 6.

possible to work with much larger quantities of lime liquor, and hence to titrate larger quantities of ammonia. If suitable indicators could be found, a rapid titration of ammonia in lime liquors might be made by testing their total alkalinity, then boiling the solution for a short time to drive off the free ammonia, and titrating again. Unfortunately the presence of amido-acids and other weakly acid bodies renders the end reaction for the total alkalinity an uncertain one with methyl orange, and phenolphthalein is not sufficiently sensitive to the action of ammonia to be employed.

Determination of Ammonia by Schloessing's Method.—25 c.c. of the liquor which has been quickly filtered into a flask from a funnel covered with a clock-glass to avoid loss of ammonia and carbonation, is placed in the lower basin of a Schloessing's apparatus (Fig. 7), and 25 c.c. decinormal sulphuric acid in the upper one, and the apparatus is closed for at least 48 (preferably 72) hours. The ammonia passes into the acid, which is titrated back with N/10 sodium hydrate or barium hydrate solution in presence of methyl orange, litmus or lacmoid

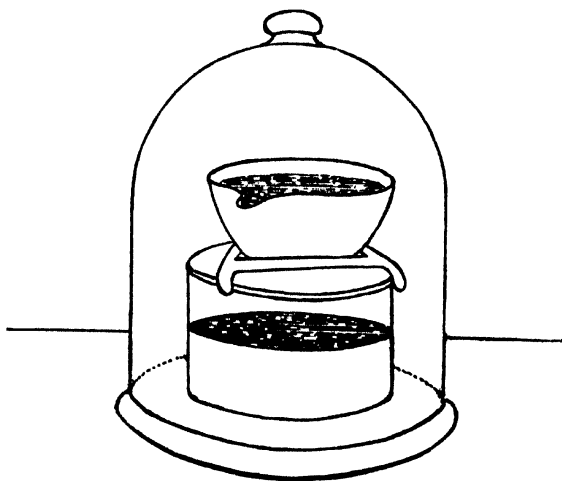


FIG. 7.

(Kathreiner), or with lime-water. A modified apparatus may be constructed by supporting a small basin or porcelain crucible in a flat-bottomed glass crystallising dish. The lime liquor is placed in the crucible, while the acid, diluted if necessary with water, surrounds it in the bottom of the crystallising dish, and forms a water-seal for a second dish, or beaker, which is inverted over the crucible. If this be placed on the top of an air bath or other warm place, the reaction will be complete in 24 hours. It is very important that both the vessels should expose as much surface as possible, and that while there should be ample space

for the ammoniacal vapour to diffuse into the acid, the capacity of the containing vessel should not be uselessly great. The closure must be accurately airtight to prevent escape of ammonia, and if ground joints are used, they must be accurate, and lubricated with vaseline. Corks, or rubber stoppers, often give off traces of ammonia, and are therefore inadmissible. A good form for the outer vessel is that of a shallow exsiccator or glass jar, with a cover ground to fit. The ammoniacal liquid is placed in the bottom of the jar, and the acid in a shallow basin, raised just above the surface of the liquid by a glass tripod.

By Distillation.—Much more rapid determinations may be made by using a conical flask or a retort of at least 500 c.c. capacity, connected with an absorption flask or U tube containing standard acid. The apparatus used in the determination of ammonia in Kjeldahl's process (p. 67) is very suitable, but it is well to introduce a wide tube filled with beads or broken glass in the limb above the boiling flask, as liquids containing organic matter are apt to froth excessively. The liquid condensing in and above this constantly washes the frothing substance back into the boiling flask. The frothing may be greatly diminished by the addition of a few drops of oil of turpentine. A suitable quantity of standard acid is placed in the absorption apparatus, and 100 c.c. of the liquor in the retort, which is briskly boiled for 15 minutes and the absorption apparatus rinsed out, and the liquid titrated back, usually with caustic alkali in presence of methyl orange. If the boiling of alkaline liquors containing nitrogenous organic matter is long continued, traces of ammonia are evolved by the action of the alkali on the organic matter present. This may be prevented or at least much lessened, if the residue is not required for the determination of caustic lime, by adding two or three c.c. of a 10 per cent. solution of $\text{MgSO}_4 \cdot 7\text{OH}_2$, which converts the alkali or alkaline earth into sulphate, setting free the MgO ; but is rarely of importance for technical purposes, if the boiling is not long continued. In liquids containing ammoniacal salts, the ammonia is best liberated by the addition of calcined magnesia, which has little or no action on organic matter, and does not affect methyl orange if carried over as spray. In comparing cold methods with distillation methods of estimating ammonia, it must be remembered that amines, if present, will be more com-

pletely estimated in the latter case on account of their lesser volatility.

In estimating ammonia by titration, indicators more sensitive to weak acids than weak alkalies, such as phenolphthalein, are unsuitable. Congo red has been a good deal used by continental chemists, but its end-reaction is not sharp. Methyl orange is better by daylight and for the trained eye, but probably carminic acid (1 per cent. aqueous solution) is to be preferred, not only on account of the sharpness of the colour-change, but because it is easily seen by artificial light.

The Kjeldahl Method of Nitrogen Determination.—The principles of this method have already been briefly alluded to. Few processes have been subject to more varied suggestion and real or supposed improvement, but, except as regards estimation of nitrogen in the form of nitric acid and nitro-compounds, which can scarcely concern the leather chemist, it is doubtful if any real advance has been made on the process as first proposed by the inventor. The essential idea of the method is the digestion of the nitrogenous organic matter with an excess of concentrated sulphuric acid, which acts not only as a dehydrating but an oxidising agent, destroying all carbonaceous matter, and transforming all organic nitrogen into ammonium sulphate. With many proteids indeed, and with hide itself, accurate results may be obtained by this simple method if the digestion is carried on sufficiently long to destroy all organic matter, and produce a perfectly colourless solution. Where, however, matters contain much carbon in proportion to nitrogen, as is the case with leather, this digestion becomes very tedious, two or three hours being often required to complete the reaction, and many suggestions have been made to shorten the time required, and render complete oxidation more certain. This may be accomplished either by the addition of more powerful oxidisers, such as the potassium permanganate employed by Kjeldahl, of oxygen carriers, such as mercury and copper, or of salts, such as potassium sulphate, calculated to raise the temperature of the boiling sulphuric acid. It must be particularly emphasised that by all these methods, carefully carried to complete oxidation and decolorisation of the solution, accurate and concordant results are obtained, and that the question to be decided is rather one of rapidity and convenience of manipulation than of exactness. There is at least a

*theoretical possibility that very strong oxidising agents may cause loss by liberation of free nitrogen, and this danger becomes probably a real one where chlorides are present from which free chlorine may be evolved. The use of metallic salts, such as the sulphates of mercury or copper, besides somewhat complicating the process, causes precipitates in the solution when rendered alkaline with soda, and increases the very annoying tendency to "bumping," always present during the distillation of the ammonia; and even the addition of a soluble salt like potassium sulphate is somewhat troublesome in the latter respect.

For the analysis of leather, Dr. Nihoul* recommends the following method as rapid and accurate: 0.6-0.7 of grm. the leather, freed from fats and water-soluble matter, is boiled for half an hour with 10 c.c. of pure concentrated sulphuric acid. The flask is allowed to cool to a moderate temperature, and a dozen large crystals of potassium permanganate are added and shaken till dissolved. The flask is then again heated till the liquid is completely decolorised, and allowed to cool. The solution is made up to 250 c.c. (including washings if it is transferred to a separate distilling flask), 150 c.c. of 30 per cent. soda solution is added, and a known quantity of zinc dust, and the distillation is continued slowly so that in $\frac{3}{4}$ hour about 200 c.c. have passed over into the receiver, which contains 25 c.c. of N/5 sulphuric acid, and the solution is titrated back in presence of carminic acid or methyl orange.

If this method is applied to actual hide-substance, the quantity of dry matter used, must not exceed 0.4 grm. In place of the permanganate recommended by Nihoul, 1 grm. of potassium persulphate, or more if required for decolorisation, may be used, and has the advantage of causing no change in the colour of the solution, and no precipitate on the addition of caustic soda.†

If the use of oxidising agents is considered objectionable, good results are obtained by the use of 15 c.c. of concentrated sulphuric acid to which, when the substance is dissolved, 10 grm. of dried and powdered potassium sulphate is added; but con-

* Bourse aux Cuirs de Liège, Sept. 1901, p. 14; Abstr. Journ. Soc. Chem., 1901, p. 1249.

† Compare Law, Journ. Soc. Ch. Ind., 1902, p. 847, and Dakin, *ibid.* p. 848. Potassium persulphate, however, usually contains traces of ammonia, which must be determined and allowed for.

siderably longer boiling is required before the liquid becomes colourless. The time is somewhat reduced by the addition of 2 grm. of dry copper sulphate * or of about 1 grm. of mercury ; but in the last case, sodium sulphide must be added with the caustic soda on distillation to decompose the ammonia-mercury compound formed.

Dr. O. Böttcher† recommends in the analysis of artificial manures, the use of a mixture of 200 grm. of phosphoric anhydride with 1 liter of concentrated sulphuric acid to which, for 20 c.c. of acid, 1 grm. of mercury and 10 to 15 grm. of potassium sulphate may be added. This quantity of mercury will require about 25 c.c. of a 4 per cent. solution of potassium polysulphide (liver of sulphur) for precipitation ; but Dr. Böttcher states that if $1\frac{1}{2}$ grm. of granulated zinc (free from arsenic) is added to the distilling flask, no sulphide is needed, and the boiling proceeds without bumping. If zinc is used for this purpose, the acid, after dilution with water, should be nearly neutralised with the soda before adding the zinc. For this purpose, it is convenient to ascertain by a rough titration what quantity of the soda solution is needed to neutralise the volume of acid employed.

As regards the apparatus employed, long-necked spherical Jena glass flasks of 100–200 c.c. capacity are most suitable for the digestion with sulphuric acid, which is done over a small flame, under a good draught, the flask being held in a clamp or on a suitable support, with its neck inclined, and closed with a glass bulb with a short sealed stem, or with a small funnel, to avoid the possibility of loss by spirting. Jena glass flasks of about 400 c.c. capacity should be used for the distillation, and hard glass, which does not yield any alkali to ammoniacal vapours, must also be selected for tubes and receivers. Care should be taken that wherever rubber tube is used for jointing, the ends of the glass tubes butt closely together so as to expose the rubber as little as possible. In place of glass flasks, copper flasks are advantageously used for distillation, and entirely avoid trouble from bumping, but are difficult to obtain without a soldered seam, which is liable to attack by the caustic alkali. If glass flasks are used, it is advisable to carry a tube drawn to a narrow point through the cork down to the bottom of the flask,

* Cp. Procter and Turnbull, *Journ. Soc. Ch. Ind.*, 1900, p. 130.

† Lunge's *Chemisch-Technische Untersuchung-Methode*, ii. 379.

and carry in a current of steam from ammonia-free water from a boiling flask to prevent bumping. In this case a condenser should also be employed. In place of steam, a current of ammonia-free air may be sucked through the apparatus. 15 to 20 minutes boiling is sufficient.

Almost every chemist has his favourite form of distilling apparatus ; but the really important point, on which the accuracy of the analysis depends, is the complete separation of the spray

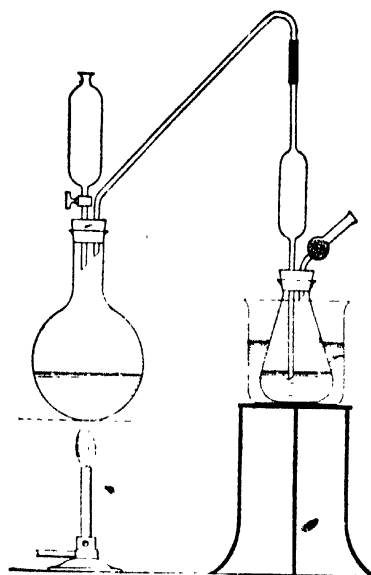


FIG. 8.

of the strongly alkaline soda-solution from the ammoniacal steam which passes into the receiver. The condensation of the steam after it has carried the ammonia into the absorbing standard acid seems unimportant, and the writer has always obtained good results with the simple apparatus shown in Fig. 8, in which the long rising tube of not less than 5 mm. bore serves at once to condense part of the water which runs back into the boiling flask, and to act as a spray-trap in which particles of spray striking the wet sides of the tube are caught by the condensed

water and washed back into the boiling flask. The bottom of this tube may be simply cut off obliquely as shown, but a better form very easy to make has a side-hole blown near the end of the tube, through which the steam and spray enter, while the end is drawn out to a small opening, through which the condensed water drips back into the flask. The stoppage of spray would be rendered still more perfect by widening the lower part of the tube and filling it with beads or broken glass, but the apparatus as figured answers every practical purpose so long as steam only has to be dealt with. If, however, hydrogen is evolved from granulated zinc, the spray is of a much more finely divided type, and many traps have been devised to remove it; but most of these are beyond the scope of the amateur glass-blower, and must be obtained of the chemical instrument maker. It is not necessary to cool the absorption-flask, if standard sulphuric acid is used to absorb the ammonia, as the latter is quite efficiently retained even by hot acid, if the point of the pipette dips very slightly below its surface. The object of the pipette, or bulbéd tube, is to prevent the standard acid being drawn back into the boiling flask by any slight condensation of steam. Many chemists, however, prefer to use a condenser, the inner tube of which may be either of glass or of pure tin, which is a better conductor of heat and is unaffected by ammonia. A small guard-tube in the cork of the absorption-flask, as shown in the figure, filled with broken glass and wet with a portion of the standard acid coloured with methyl orange, prevents danger of escape of ammonia unabsorbed. It is, of course, rinsed into the flask before titration.

To sum up, the simplest form of process, that of digestion with sulphuric acid alone, is to be preferred for substances which it will oxidise within a reasonable time. It is sometimes necessary if the digestion is long continued, to make up for loss of sulphuric acid by a further addition. The use of potassium sulphate to raise the temperature is quite unobjectionable if the solution be freely diluted before distillation, and if it be necessary to further shorten the time by the use of an oxidising agent, potassium persulphate is ideal if it can be obtained free from ammonia; and potassium permanganate, though less convenient, is also satisfactory, but in no case should an oxidising agent be added till solution is complete, and the digestion well advanced. Where many analyses are made, copper flasks are strongly to be

advised for distillation, in which case a condenser is unnecessary, but if glass flasks are employed the use of a current of steam and a condenser is advisable.

As the calculation of Kjeldahl estimations is slightly complicated, it may be well to give an example. 0.7 gm. of leather has been taken, and 5 c.c. of N/5 caustic soda has been required to titrate back the 25 c.c. of N/5 acid placed in the absorption-flask. Each c.c. of N/5 acid corresponds to 0.0034 gm. NH_3 ; to 0.0028 gm. N; or to 0.01573 gm. of hide-substance reckoned to contain 17.8 per cent. of nitrogen.* Taking the latter figure, we have—

$$\frac{20 \times 0.01573 \times 100}{0.7} = 44.95 \text{ per cent. of hide-substance;}$$

and, of course, the nitrogen or the ammonia can be obtained in a similar way by using the corresponding factors.

SECTION VI.

THE MATERIALS USED IN CURING, BATING, ETC.

Common Salt ($\text{NaCl} = 58.5$).—This material is so cheap that it is not likely that it will be purposely adulterated, but may contain accidental impurities. Moisture may be determined by heating a few grams to 110°C . or over, in a crucible or basin which should be at first covered to avoid loss by decrepitation. Insoluble impurities are detected by dissolving say 10 gm. in water; and may be collected on a tared filter, washed, dried at 110° , and weighed, and afterwards ignited to determine organic matter by loss. The residue, if brown or yellow, probably contains iron, which may cause stains on leather, and both residue and solution should be tested for ferric salts with thiocyanate, if necessary after solution in HCl and oxidation with a little nitric acid. The iron may be estimated colorimetrically (p. 40) as in water.

Salt not unfrequently contains magnesian and sometimes calcic

* Von Schroeder for hide-substance, the following percentages of N. Ox, calf, horse, camel, pig, rhinoceros, 17.8; goat and deer, 17.4; sheep and dog, 17.0; cat, 17.1.

chlorides as impurities, which tend to make it absorb moisture which for some purposes is objectionable. These salts also lose hydrochloric acid on ignition. To determine these impurities, a known quantity, say 10 grm., is dissolved in 100 c.c. of water; insoluble impurities if present are filtered off as above described, and the filter is washed, the solution boiled with a few drops of nitric acid, ammonium chloride and ammonia are added, and ferric oxide and alumina filtered off, and estimated if present (p. 44). Ammonium carbonate and a little ammonium oxalate are now added, and the mixture boiled, and, if any precipitate forms, allowed to stand 24 hours, the lime estimated as on p. 45; and the magnesia is then precipitated from the filtrate with sodium phosphate, and estimated as pyrophosphate (p. 45).

A simpler method where magnesia only is to be estimated, is to precipitate the MgO with excess of lime-water as in the case of water analysis (p. 36). To 100 c.c. of solution containing 10 grm. of salt, made with water well boiled to expel CO_2 , and quite neutral to phenolphthalein, 100 c.c. of lime-water are added, the strength of which has been accurately determined with $N/10$ HCl and phenolphthalein. The mixture is allowed to stand overnight or heated in the water-bath for half an hour and allowed to cool and settle quite clear, when 50 c.c. are drawn off repeatedly and titrated. If 100 c.c. of the lime-water require 48 c.c. of $N/10$ acid, and the 200 c.c. of mixture, as calculated by multiplying the average result of 50 c.c. by 4, require 18 c.c., the result is $(48 - 18) \times 10 \times 0.002 = 0.6$ per cent., the $N/10$ acid corresponding to 0.002 grm. of MgO or 0.00475 of $MgCl_2$ per c.c. The quantity of lime-water used must be such that the solution remains deeply coloured with the phenolphthalein after standing.

The chlorine may of course be determined with argentic nitrate as on p. 39, but this is rarely necessary except for the estimation of small quantities of salt in wash-waters and the like.

The specific gravity of salt solutions of different strength is given in the following Table. Salt is only soluble in water at 15° to the extent of 26.4 per cent. by weight, or 318 grm. per liter, and the solubility only increases slowly with temperature, rising to 28.9 per cent. at 109.7° , the temperature of boiling salt solution, and falling to 24.5 per cent. at 14° , its freezing point.

THE MATERIALS USED IN CURING, BATING, ETC. 71

Between 0° and 25° it remains almost constant at about 26.4 per cent., and 1000 parts of water dissolve 369 parts of salt. Baumé degrees correspond very approximately to the percentage of salt.

SPECIFIC GRAVITY OF SODIUM CHLORIDE SOLUTIONS
AT 15° C. (59° FAH.). (Gerlach.)

Sp. Gr.	Percentage Salt.	Sp. Gr.	Percentage Salt.	Sp. Gr.	Percentage Salt.
1.00725	1	1.07335	10	1.14315	19
1.01450	2	1.08097	11	1.15107	20
1.02174	3	1.08859	12	1.15931	21
1.02899	4	1.09622	13	1.16755	22
1.03624	5	1.10384	14	1.17580	23
1.04366	6	1.11146	15	1.18404	24
1.05108	7	1.11938	16	1.19228	25
1.05851	8	1.12730	17	1.20098	26
1.06593	9	1.13523	18	1.20433	26.395

Ammonium Salts and Ammonia.—So-called "ammonia" or "liquid ammonia" is a solution of NH_3 (or NH_4OH) in water. Real liquid ammonia is NH_3 gas liquefied by pressure, and is now largely used in ice machines, and for other purposes. Beside ammonia, the most important compounds are sulphate and chloride.

The strength of ammonia solution is usually calculated from its specific gravity, which may be taken with the pycnometer or by means of a suitable hydrometer. A scaled glass bulb, loaded with mercury so as just to float in a solution of the required density, is a convenient and delicate means of making a solution of constant strength. Strong solutions lose strength rapidly and serious damage has been done to leather by not allowing for the greater strength of a fresh solution. The strongest commercial ammonia contains about 33 per cent. of NH_3 , corresponding to a density of 0.886, and may be conveniently diluted with twice its bulk of water, which will give a gravity of about 0.956. It should be kept in carboys as closely stoppered as possible. The following table, abridged from Lunge and Wiernik, gives the weight of NH_3 contained in 100 grm. and 100 c.c. of liquid ammonia at different specific gravities taken at 15° C.

Specific Gravity at 15° C.	Grms. per 100 grms.	Grms. per 100 c.c.
1.000	0.00	0.00
0.990	2.31	2.29
0.980	4.80	4.70
0.970	7.31	7.09
0.960	9.91	9.51
0.950	12.74	12.10
0.940	15.63	14.69
0.930	18.64	17.34
0.920	21.75	20.01
0.910	24.99	22.74
0.900	28.33	25.50
0.890	31.75	28.26
0.882	34.95	30.83

The strength of ammonia (previously diluted with water if strong) is also determined easily and exactly by titration with standard hydrochloric or sulphuric acid, with carminic acid, methyl orange or litmus (not phenolphthalein) as indicator. Each c.c. of N/1 acid corresponds to 0.017 gm. of NH_3 . The ammonia of ammonium salts is similarly determined by liberating with caustic alkali or lime, and distilling into a known volume of standard acid, which is afterwards titrated back with standard sodium carbonate. Each c.c. of N/1 acid corresponds to 0.0535 gm. of NH_4Cl , or 0.066 of $(\text{NH}_4)_2\text{SO}_4$. The apparatus described for ammonia determination by distillation in Kjeldahl's method (p. 67), or a simple flask connected with a capacious U tube may be employed. Excess of soda solution may be run in from a tapped separating funnel, as shown in Fig. 8, or stick soda or potash sufficient to render the solution strongly alkaline may be dropped in wrapped in filter paper, and the apparatus rapidly closed to prevent loss. Liquids containing ammonia with organic matters should be treated like lime liquors, and if necessary free ammonia may be determined by simple distillation, and alkali then added to decompose the salts, and the distillation continued. Where lime or caustic alkalies are objectionable, magnesia may be used to liberate ammonia. Ammonia in waters and extremely dilute solutions may be estimated by Nesslerising instead of titration.

Sulphurous Acid and Sulphites.—For ordinary alkalimetical estimation, see p. 27. They may also be estimated by oxidation with iodine as follows:—

About 0.5 gm. of powdered sodium sulphite, or an equivalent portion of other salts or liquids, is introduced at once into a beaker containing excess (40 c.c.) of N/10 iodine solution, stirred till dissolved, and the solution is at once diluted with water and titrated back with N/10 sodium thiosulphate, as described on pp. 258 and 306. Under these circumstances the SO_2 is oxidised completely to sulphuric acid, while if the iodine solution is added gradually to the sulphurous acid or sulphite, the reaction is irregular and incomplete. If it is found that considerable excess of iodine solution has been used, it is desirable to repeat the experiment with such proportions of the sulphite and iodine solution as will leave but slight excess of the latter. One c.c. of N/10 iodine solution is equivalent to 0.0032 gm. of SO_2 ; 0.0126 gm. of cryst. sodium sulphite, $\text{Na}_2\text{SO}_3 + 7\text{Aq}$; and 0.00475 gm. of sodium anhydrosulphite (Boake's "metabisulphite"), $\text{Na}_2\text{S}_2\text{O}_5$.

Giles and Shearer† have also investigated the specific gravity of sulphurous acid solutions, with the result that it is practically directly proportional to the strength, each per cent. of SO_2 corresponding to an addition of 0.005 to the gravity; or in other words, that each degree Tw. corresponds to 1 per cent. of SO_2 with very considerable exactness. In the original article a table is given. The similarity of sulphurous to hydrochloric acid* (p. 24) in this respect is worth noting. A saturated solution at ordinary temperatures contains about 10 per cent. of SO_2 .

Sulphurous acid, while somewhat costly to buy, from the dilute character of its aqueous solution and consequent cost of transport, is one of the cheapest of acids to make by combustion of sulphur.‡ For use in small quantities, the compressed liquid acid in siphons is very convenient, and on a larger scale Boake's "metabisulphite" (see above) may often be advantageously employed, as it contains 67.3 per cent. of its weight of SO_2 , which can be liberated by the addition of 1 mol. of sulphuric acid (98), or 2 of hydrochloric (73), to 1 mol. of the salt (190), practically 1 part of sulphuric acid sp. gr. 1.84 (164°Tw.) or 2 parts of hydro-

* Cp. Giles and Shearer, J. S. C. I., 1884, p. 197; 1885, p. 303.

† Loc. cit.

‡ Principles of Leather Manufacture, p. 24.

chloric acid sp. gr. 1.17 (34° Tw.) will decompose 2 parts of metabisulphite, leaving only sodium sulphate or chloride. A solution of 1 per cent. of sodium metabisulphite and 0.5 per cent. of sulphuric or 1 per cent. of hydrochloric acid answers well for bleaching and removing iron stains from leather, though its action is rather slow, about 12 hours' soaking being necessary. With the addition of 10 per cent. of salt, the same solution may be used for removing iron-stains (so-called "salt-stains") from untanned pelt, but some salt must be added to the early liquors. The operation is best carried out in a closed drum.

Boric (Boracic) Acid and Borates.—These substances are coming into extended use in leather manufacture, not only as antiseptics but as deliming agents. Boric acid forms compounds with lime, soluble in dilute solutions, and is one of the safest chemical "bates." * It also exercises a peculiar and little understood effect on skins in tanning liquors, giving good colour and preventing "drawn grain" in the early stages of tanning, even when green goods are introduced into comparatively strong liquors; but if continued throughout the process producing soft and light-weighting leather. This property is probably connected with the power of boric acid to form conjugated acids with tannins and their derivatives, as well as with other phenolic compounds.

Boron, B = 11, is tribasic, forming the oxide B_2O_3 and the very weak acid $B(OH)_3 = 62$, known as boric or boracic acid. This acid, which appears to be dibasic, but forms no stable salts, is converted into metaboric acid HBO_2 by heating to 100° C., at which temperature it is slowly volatile. On heating to 140° C., it very slowly parts with more water and becomes pyroboric acid, $H_2B_4O_7$, a glassy mass which on ignition to redness is converted into B_2O_3 . Both metaboric and pyroboric acid form salts, the former being monobasic and the latter dibasic, but both acids are weaker than carbonic. Borax is a pyroborate, and a calcium metaborate is known, $Ca(BO_2)_2$, which is somewhat soluble in water, like all other known metallic borates.

Detection.—Free boric acid in either aqueous or alcoholic solution turns turmeric paper a reddish brown somewhat different

In the use of boric acid as a deliming agent it is necessary to avoid the accumulation of lime borates, with which the solution soon becomes saturated, and is then, in spite of excess of boric acid, unable to remove lime, but fixes it in the pelt.

to that produced by alkalis, and unlike the latter, blackened by acids instead of being discharged. Free boric acid is soluble in alcohol, and can consequently be separated from sulphates and many other matters by digestion with alcohol, to which the turmeric test is applied. Boric acid, though capable of withstanding the heat of the blowpipe in the dry state, is decidedly volatile when solutions in water are evaporated, and still more so with methyl and ethyl alcohols, with which it forms volatile methyl and ethyl borates or esters. Solutions containing it must therefore be neutralised or rendered slightly alkaline before evaporation to avoid loss. In presence of soda or sodium carbonate it may be safely evaporated and even ignited. Small traces of the acid can be detected by taking the ignited residue and slightly acidifying with sulphuric acid in a test-tube. A little alcohol is now added, and the mixture is boiled and the escaping vapours are ignited. In presence of boric acid the edges of the flame are coloured green. Somewhat similar coloration may be produced by the presence of copper salts, or by ethylic or methylic chlorides produced by the action of concentrated hydrochloric acid on alcohols; but in the latter case the flame is a bluer green than that of boric ester. If the traces of boric acid are too minute to be detected even in this way, they may still be separated by distillation as described below, and then tested for with turmeric or the alcohol flame.

Quantitative Determination.—It has been noted that boric acid, like carbonic acid, does not redden methyl orange, and the whole of the base in alkaline borates, such as borax, may be estimated with standard sulphuric or hydrochloric acid by the aid of this indicator, or of lacmoid paper, precisely as in the case of carbonates (p. 28). Borax (crystallised sodium pyroborate, $\text{Na}_2\text{B}_4\text{O}_7 + 10\text{Aq} = 382$) often called "biborate," has been proposed as a basis for alkalimetical solutions in place of sodium carbonate, but is only soluble in cold water to the extent of about 60 grm. per liter. 19.1 grm. per liter forms a solution N/10 to acids with methyl orange as indicator. It has been stated by Dr. L. Spiegel* that it is occasionally, though rarely, contaminated with triborate, but this is somewhat doubtful.

Boric acid gives no defined end-reaction with phenolphthalein, but on adding neutral glycerin, a conjugated acid is formed

* Chem. Zeit., 1904, p. 730.

to which the indicator is very sensitive, and advantage is taken of this fact in estimation. One curious result is due to this property. If glycerin is added to a solution of borax, which is distinctly alkaline to litmus, the reaction becomes acid. The formation of a similar compound with phenol is probably the cause of the very satisfactory deliming action of a solution containing 2 per cent. of boric acid and 1 per cent. of phenol, noted by Parker and Procter.* A saturated aqueous solution of boric acid and phenol is a useful antiseptic, which may be used for washing hands or applied to cuts and abrasions where septic poisoning may be feared.

For the determination, 50 c.c. of the boric solution, which may contain 30–40 grm. borax or 10–15 grm. boric acid per liter, is carefully neutralised in presence of methyl orange, with sulphuric or hydrochloric acid if alkaline, or with caustic soda free from CO_2 if acid, and is then boiled to expel carbonic acid if its presence is suspected. 30 c.c. of glycerin (previously neutralised, if necessary, with caustic soda) is now added, and the solution is titrated in presence of phenolphthalein with $\text{N}/2$ or $\text{N}/10$ NaOH (perfectly free from CO_2), till a pink tint is produced. 10 c.c. more glycerin is now added, when in some cases the pink colour will disappear, and more soda must be added to bring it back, and the addition of soda and glycerin alternately must be continued till the pink remains permanent. Under these conditions the end-reaction is quite sharp, and the alkali consumed corresponds to the equation $\text{B}_2\text{O}_3 = 2\text{NaOH}$; or each c.c. of $\text{N}/1$ alkali corresponds to 0.035 grm. B_2O_3 , or 0.062 grm. $\text{B}(\text{OH})_3$, or 0.0956 grm. of borax. If borax is titrated in this way without previous neutralisation to methyl orange, only half this quantity of acid will be consumed, or 1 c.c. will correspond to 0.191 grm., as in the case of alkalimetric determination.†

In the titration of boric acid solutions which have been used in deliming hides, only approximate results can be obtained from the presence of lime-salts of weak organic acids which render the end-point with methyl orange indistinct. These may be destroyed by evaporation to dryness and ignition.

In many cases it is desirable to separate boric acid from other

Journ. Soc. Chem. Ind., 1895, p. 124. This book, p. 239.

† Cp. Hönig and Spitz, Zeits. f. ang. Chem., 1896, p. 549; Journ. Soc. Chem. Ind., 1896, p. 742; Thomson, *ibid.*, 1895, p. 1070.

matters before determining it by titration or otherwise, and this is most conveniently achieved by taking advantage of its volatility when boiled with alcohols. The substance is freed from organic matter by rendering alkaline with sodium hydrate or carbonate, evaporating to dryness, and igniting. It is then powdered, and rendered slightly acid with sulphuric acid, and digested with 100 c.c. of absolute alcohol in a flask with reflux condenser. The solution is then distilled into a flask containing 20 c.c. of N/1 sodic hydrate free from CO_2 . The last drops of the distillate are tested with turmeric paper for boric acid (alcohol alone gives a darkened yellow edge to the spot, but no red coloration), and if any trace is observed, 25 c.c. more alcohol are added to the residue, and the distillation continued till all boric acid has passed over. The boric acid flask should be immersed in the water or steam bath up to its neck, so as to prevent condensation before the boric acid vapour reaches the condenser. The quantities given should suffice if the residue treated does not contain more than 0.5 grm. of boric acid. Where the quantity of foreign matter is considerable, it is better to filter off and distil the alcoholic extract only, after washing the residue with hot alcohol. The alcohol is now distilled off the receiving flask, leaving the boric acid in combination with the soda, which can be estimated by titration as above described. A less quantity of alcohol may be used, if it is distilled backwards and forwards between the two flasks by changing their positions and heating them alternately, but in this case it is desirable to use an equivalent quantity of a concentrated solution of soda, instead of the normal solution, to avoid dilution of the alcohol. By heating both the flasks, and connecting them with two condensers sloping in opposite directions, and somewhat contracted at their lower ends so that a drop of condensed liquid hangs in the end of the tube and checks entrance of the vapour in the wrong direction, both distillations can be conducted simultaneously; and in this case the substitution of 25–50 c.c. of methyl-alcohol for the ethyl-alcohol is advantageous. The connection with the return-flow condenser should not be quite air-tight, so as to avoid risk of explosion. One hour and a half is said to be enough for the distillation of 0.3 grm. of boric acid.*

* Cp. Jay and Dupasquier, *Comp. Rend.*, cxxi. p. 260; *Journ. Soc. Chem. Ind.*, 1895, p. 889; 1896, p. 136; and Dr. Schneider, *Ch. Zeit.*, 1896, p. 822.

Carbolic Acids and Creolins.—Pure phenol, "pure crystallised carbolic acid," is hydroxy-benzene $C_6H_5(OH)$, but the crude forms which are generally employed contain cresols and other higher members of the series in which one or more atoms of hydrogen are substituted by CH_3 groups. These are oily bodies sparingly soluble in water, and even pure phenol is only soluble to the extent of about 7 per cent. Crude carbolic acid should not be employed in the tannery, since the insoluble oily particles stain the hide and render it insusceptible of tanning. Suitable carbolic acid should be of a pale yellow colour when fresh (though it will darken on exposure to air and light), and it should be wholly soluble in a sufficient quantity of water. Its specific gravity should be 1.050 to 1.065.

The actual analysis of crude carbolic acids is beyond the scope of this book, but the following tests, described by Allen,* will give an approximate idea of their value. They consist mainly of phenol and its higher homologues, but frequently contain water and neutral tar-oils of little direct value as antiseptics.

Determination of Water.—20 c.c. of the carbolic acid are agitated in a stoppered graduated cylinder or corked tap-burette with 10 c.c. of saturated salt solution. The water will pass into the salt solution and the volume may be read off. The whole of the water is not actually removed: pure anhydrous phenol actually absorbs a small portion of the water, precipitating salt. The volume of 10 gramm. of pure crystallised phenol, after shaking with salt solution, is about 9.7 c.c., from which the actual weight of the anhydrous phenols may be inferred, though their specific gravity will be somewhat greater than that of pure phenol.

Determination of Neutral Oils.—10 or 20 c.c. of the carbolic acid are agitated with twice its volume of a 9 per cent. solution of caustic soda free from alumina. The phenol and cresols will dissolve, and the neutral oils will remain floating on the aqueous layer if "light," and sinking below it if "heavy." Their volume may now be noted. The addition of 10 c.c. of petroleum spirit facilitates their separation, and causes them to float. The volume of spirit added must, of course, be deducted from the reading.

Creolin (Jeyes' Fluid) and similar disinfectants, which are

emulsions of the heavier homologues of phenol with soap or an alkali, may be similarly examined by adding sufficient normal acid to reddien methyl orange to 20 c.c. in a burette, and then saturating with salt, when the phenols and cresols will separate in oily drops.* The acid is run off by the tap, and the cresols washed with saturated salt-solution, which is added to the acid, and titrated back with normal soda, when the loss will correspond to the alkali originally present. The neutral oils may be determined as in carboic acid, but often separate with great difficulty.

Formaldehyde ($H.CHO = 30$).—The simplest member of the aldehyde series, obtained commercially by the oxidation of methyl-alcohol, CH_3OH , and now used largely both as a disinfectant, and as a tanning and hardening agent for skin and other gelatinous substances, which it renders insoluble even in hot water. It is usually sold as an aqueous solution of approximately 40 per cent. strength under the names of "formaline," "formol," etc., the pure substance being gaseous at ordinary temperatures, but readily polymerising or combining with itself to form a white crystalline body, tri-formol or paraform, $C_3H_4O_3$, which sublimates at $100^\circ C.$, and is decomposed again into formaldehyde at somewhat higher temperatures. This body is frequently formed as a white sediment in formaldehyde solutions. The specific gravity of formaline varies from 1.08 to 1.09, not only from the percentage of formaldehyde, but from that of methyl-alcohol, which is frequently present to the extent of 15–20 per cent., either as an impurity of manufacture or to prevent precipitation of tri-formol.

Both as a bactericide, and in its hardening action on gelatine and animal tissues, formaldehyde is extremely powerful. It is stated that 1 part of formaldehyde or $2\frac{1}{2}$ parts of formaline in 12,000 parts of water is sufficient to sterilise, while in Payne and Pullman's tanning process* a solution of $2\frac{1}{2}$ parts of formaline in 1000 of water rendered alkaline with sodium carbonate will convert hides into leather in a few hours. In acid solution it has the power of fixing hide in a swollen condition and allowing of very rapid tannage with vegetable materials. This hardening and tanning action seems to be common to all aldehydes in a greater or less degree.

Detection.—Aldehydes in general are usually easily detected

* Principles of Leather Manufacture, p. 380.

by their power, even when present only in traces, of reddening a solution of rosaniline previously acidified, and nearly decolorised by addition of sodium sulphite (Schiff's reaction). This property is common to all aldehydes, including acetaldehyde, chloral (but not chloral-hydrate), benzaldehyde, furfural, acrolein, etc., and is slightly produced by some alcohols and by acetone, but not by most other ketones. It is, therefore, not absolute proof of the presence of formaldehyde, and it also seems incapable of detecting it in actual combination with gelatinous matter, though most leathers which have been treated with formaldehyde retain enough in a free state to give the reaction readily. It must be remembered that oil- and chamoised leathers may react from the presence of acrolein (acrylic aldehyde), which is probably the active agent in oil-dressing.

Nierenstein has also shown* that most tanning infusions give a red coloration with it on standing, from the reduction to aldehydes of the tannin-acids by the sulphurous acid present. The colour of the reagent also reappears by oxidation and loss of SO_2 on exposure to the air.

The reagent is in the author's experience most conveniently prepared by passing SO_2 very slowly into a 0.025 per cent. solution of magenta till it is just decolorised, and may be kept for a considerable time.

At the author's request, Dr. Nierenstein has examined the most important qualitative methods for the detection of aldehydes, and gives the preference † to Lebbin's, ‡ but with the modification of employing phloroglucol instead of resorcinol. This test is carried out by adding to a few c.c. of the liquid to be examined 2-3 c.c. of a $\frac{1}{2}$ per cent. solution of phloroglucol, or a small trace of the dry substance on the point of a penknife, rendering alkaline with 5 or 10 drops of caustic soda or potash solution, and boiling (rapidly in order to prevent darkening by oxidation). Formaldehyde gives a brownish-red, and acrylaldehyde a blue-green coloration, so that they are readily distinguished. The reaction is considerably less sensitive than that of Trillat, § but is much less tedious in execution. Trillat's reaction is obtained by adding 0.5 c.c. of the purest dimethylaniline (boiling between 190° and

* Collegium, 1905, p. 159.

† Ibid. 1905, p. 158.

‡ Lebbin, Chem. Centralblatt, 1896, ii. 930.

§ Comp. Rend., 1898, 127, 132.

THE MATERIALS USED IN CURING, BATING, ETC. 11

191°) to 10 c.c. of the suspected liquid, acidifying with sulphuric acid and shaking thoroughly. The liquid is now rendered alkaline with sodium hydrate, boiled till free from smell of dimethylaniline, and the precipitated tetramethyldiamidodiphenylmethane is collected on a filter, washed, and treated in a small porcelain basin, first with acetic acid and then with a little finely powdered lead peroxide, when a blue colour is produced.

Quantitative Estimation of Formaldehyde.—For general use where accurate results are required, and in absence of bodies which reduce iodine, such as thiosulphates, sulphides and sulphites, tannins and the like, Romijn's method* is one of the most satisfactory and rapid, especially for dilute solutions. It depends on the oxidation of the formaldehyde to formic acid, according to the equation: $\text{H} \cdot \text{CHO} + 2\text{NaOH} + 2\text{I} = \text{HCOOH} + 2\text{NaI} + \text{OH}_2$; and hence each molecule of formaldehyde requires 2 molecules of iodine for oxidation, and each c.c. of N/5 iodine, or indirectly of thiosulphate, is equal to 0.003 grm. (1 molecule) of $\text{H} \cdot \text{CHO}$. The formaldehyde solution must not exceed about 2 per cent. in strength, and therefore 5 c.c. of 40 per cent. "formaline" must be diluted to 100 c.c. with distilled water, and well mixed by shaking.

N/5 iodine solution is made by dissolving 12.685 grm. of pure iodine (if necessary obtained from the commercial by sublimation with a little potassium iodide) with 18 grm. of pure potassium iodide in about 250 c.c. water and making up to, 500 c.c. The iodide must be free from iodate, which may be tested for by dissolving a little in water and acidifying with hydrochloric acid, when the solution will become yellow and give the usual blue reaction with starch if iodate be present. A N/10 solution of sodium thiosulphate is also made by dissolving 24.83 grm. of the pure salt, and making up to 1 liter, which must exactly correspond to the N/10 iodine solution. The accuracy of the thiosulphate solution, and indirectly that of the iodine, may be tested against a standard solution of potassium bichromate, (see p. 259). The thiosulphate is best kept in the dark, and is liable to deposit sulphur and diminish in strength if kept more than a few weeks. Instead of thiosulphate, a N/10 solution of sodium arsenite may be used, which is not liable to change, but is very poisonous.

* Zeit. Anal. Ch., 1897, No. 36, pp. 18, 21.

To make the estimation, 5 c.c. of the diluted formaldehyde solution and 30 c.c. of N/1 NaOH solution are measured into a bottle of about 500 c.c. capacity, and with a well-fitting stopper, and 70 c.c. N/5 iodine solution is added from a burette with constant shaking. The bottle is closed and again well shaken and allowed to stand for 10 minutes, when it is acidified with 40 c.c. of N/1 HCl, and titrated back with N/10 thiosulphate solution, a little starch-paste being added as the yellow ceases to be distinct, and the end-point being that at which the blue of the starch first completely disappears.

70 c.c. of the N/5 iodine solution corresponding to 140 c.c. N/10 thiosulphate have been used and supposing 73.3 c.c. of the latter are required for titration back, iodine equal to 66.7 c.c. of the N/10 thiosulphate or 33.4 c.c. of N/5 iodine have been consumed, equal to $33.4 \times 0.003 = 0.1$ gm. of formaldehyde, or if 5 c.c. of a solution of formaldehyde diluted 5 : 100 have been employed

$$\frac{33.4 \times 0.003 \times 100 \times 100}{5 \times 5} = 40.04 \text{ per cent.}$$

It is necessary to employ considerable excess of iodine to insure complete oxidation of the formaldehyde. It is safest to compare the iodine solution direct with that of thiosulphate or arsenite at the time of making the estimation, and take any little inaccuracy into calculation, and the addition of the NaOH and HCl should not affect this result. If many estimations have to be made, a N/5 solution of thiosulphate may be conveniently substituted for the N/10, which, however, is more generally useful. Starch paste is best made as required, and only a minute quantity is added to the solution towards the end of the reaction.

In cases where the use of iodine is impracticable from the presence of other reducing substances, the method of Blank and Finkenheiner* dependent on the oxidation of formaldehyde to formic acid in alkaline solution by hydrogen peroxide may sometimes be employed, and is of equal accuracy to the preceding; but the presence of other substances giving acid products under oxidation must be guarded against, and it is less adapted than Romijn's for the determination of very minute quantities. 3 gm.

* Berichte 1898, 2979.

of the (approximately 40 per cent.) solution* are weighed into a tall conical (Erlenmeyer) flask with 25 c.c. of double-normal NaOH solution, and 50 c.c. of 2.5-3.0 per cent. hydrogen peroxide previously neutralised with NaOH are slowly added during about three minutes; and the mixture is allowed to stand at least half an hour, and is then titrated back with double-normal H_2SO_4 or HCl in presence of phenolphthalein. If 30 c.c. of the 2N sulphuric acid are required to neutralise the soda, 20 c.c. of the latter have been consumed by the formic acid formed and, multiplied by 2, give 40 per cent. as the strength of the formaldehyde solution, the calculation being

$$\frac{(50 - 30) \times 2 \times 0.03 \times 100}{3}$$

Of course, if a larger or smaller volume or weight than 3 grm. or c.c. have been employed, it must be substituted for 3 in the divisor. It must be borne in mind that in all cases of analysis, if a liquid has been measured instead of weighed, the result will be obtained in grm. per 100 c.c. and must be multiplied by the specific gravity to get percentage by weight.

Another method, probably less accurate than the preceding, but very convenient as a test for commercial formaline, was first published by Lemme,† but had been long previously used by E. M. Payne as a general method for the estimation of aldehydes. It depends on the power of aldehydes to combine with bisulphites, which in the case of formaldehyde, acetaldehyde, and many others, is sufficiently strong to decompose neutral sodium sulphite, setting free sodium hydrate, according to the equation, $\text{H}.\text{CHO} + \text{Na}_2\text{SO}_3 + \text{OH}_2 = \text{CH}_2\text{OHNaSO}_3 + \text{NaOH}$. To 60 c.c. of a solution of pure $\text{Na}_2\text{SO}_3 \cdot 7 \text{ Aq}$ of 250 grm. per liter, a few drops of phenolphthalein solution are added and the red colour produced is just barely discharged by the careful addition of H_2SO_4 or HCl; 3 c.c. or 3 grm. of the formaline are now added, when the red colour will return, and must be again discharged with N/1 acid. As each c.c. of the latter corresponds to 0.03

* Fresenius and Grünhut, Zeits. f. Anal. Ch., 44, 1905, 13-24, recommend weighing in a tube which is introduced upright into the Erlenmeyer flask which already contains 25-30 c.c. of double-normal NaOH, and there upset and mixed, immediately adding the H_2O_2 as above described. They recommend litmus or azolitmin as indicator.

† Ch. Zeit., 1903, 896.

gram. of H.CHO , the percentage either on volume or weight will correspond directly to the number of c.c. used.

Where formaldehyde cannot be estimated or detected in the original mixture in which it exists it may be separated by distillation, preferably with a little dilute sulphuric acid to decompose proteid compounds. The cooling must be good and the distillation carried nearly to dryness, if the results are to be at all quantitative, though a good deal of the formaldehyde comes over in the early stages. Formaldehyde leathers should be digested for 1-3 hours with 1 c.c. of $\text{N}/10$ sulphuric acid, and 20 c.c. of water on the water-bath, either in a closed flask, or connected with the condenser. A good criticism on the various methods of estimating formaldehyde by Wallnitz is contained in Collegium, 1903, pp. 105, 115.

"*Coal-Tar*" Bates.—Several derivatives of coal-tar products have been used for deliming purposes, for which, but for cost, they are well adapted. Carboic acid (phenol) has considerable effect in removing lime, and has been used for that purpose (p. 239) by Parker and Procter, especially in connection with the colour-testing of liquors. Sulphonated derivatives of naphthalene, phenanthrene, and other hydrocarbons, probably obtained by treating the heavy, or "dead," oils of coal-tar with concentrated sulphuric acid, have been put on the market by the Martin Dennis Co., and by Hauff, of Feuerbach. The latter firm also introduced "cresotinic acid," a mixture of impure homologues of salicylic acid; and also some allied derivatives of the naphthalene series. Most of these compounds possess very pronounced antiseptic powers, and hence may be usefully employed for deliming sole leather hides in hot weather, when otherwise putrefactive changes are liable to interfere with swelling in the liquors.

Owing to the varied character of these materials it is obvious that no general directions can be given for their chemical examination.

SECTION VII.

CONTROL METHODS FOR LIMING, BATING, ETC.

IT is becoming recognised that no processes of the tanner are more important and more in need of exact scientific control than those which precede the tanning proper, for which they prepare the skin by removal of hair and certain portions of the cementing substance of the fibres, and by bringing the latter into suitable conditions of swelling and hydration for the particular sorts of leather which are required. Unfortunately the scientific methods of control with which we are acquainted still leave much to be desired, but an effort will be made in the following section to point out what can already be accomplished.

Soaks and Soaking.—Estimation of dissolved organic matter, and ammonia may be made as in limes, but if total ammonia is to be estimated, it must be set free from its salts by addition of calcined magnesia. Peptones may be estimated by precipitation (see pp. 89, 90). Mineral salts will be found which have been used in curing. Sodium (and possibly calcium and magnesium) chlorides and sulphates, sodium hydrate, sulphide, and carbonate, boric acid or borates, and arsenic are all probable. Arsenic may be looked for by the ordinary Marsh test. Many of the salts named have a solvent action on hide-substance, especially in medium dilutions, and their concentrated solutions interfere with proper swelling.

Limes and Liming.—The examination of lime itself has been described on p. 54. The total caustic lime present in a lime-liquor or sludge is easily estimated by titration with standard hydrochloric acid with phenolphthalein as indicator, the ammonia being generally negligible in comparison with the lime, or expelled by a short boiling. Very exact results are not to be expected in the case of old lime-liquors, which contain weak organic acids and bases which render the change of colour of the indicator less sharp. Where much carbonate is present, as in the case of lime sludge, the material must be freely diluted with water, and the titration done with sufficient stirring and somewhat slowly.

Where soda or sodium sulphide is used in the limes, caustic soda may be present in the lime-liquors, and will be estimated as lime. Before it could be accurately separated from lime, it would probably be necessary to destroy organic matter by evaporation to dryness and ignition, but a filtered lime-liquor may generally be assumed to be a saturated solution of caustic lime, the strength of which is given on p. 54, and therefore anything over about 1.3 grm. per liter may be reckoned as caustic soda, ammonia, or some other alkali more soluble than lime. Accumulations of caustic soda are liable to occur in limes which are used for reliming skins or hides which have been depilated with sodium sulphide, and if not watched, may lead to disastrous results. Such cases are usually best dealt with by making new limes at frequent intervals, but the addition of calcium chloride will remove caustic soda by converting it into chloride, and regenerating caustic lime, as in the Paync-Pullman liming process. For this reason it is sometimes useful to add calcium chloride to limes in which sodium sulphide is used if it is desired to avoid swelling, and by doing so, the effects of arsenic-limes may be closely imitated by the much cheaper and safer sodium sulphide.

Considerable quantities of lime are contained in lime-liquors in clear solution neutral to phenolphthalein in combination with organic matter. The *total lime* present is easily estimated by evaporating a measured quantity of the filtered liquor to dryness, weighing the total solids, igniting, and weighing the ash as calcium carbonate (see p. 45), after moistening with ammonium carbonate, and again gently igniting. If other mineral matters are present the residue of carbonates from the ignition of organic matter may be dissolved in hydrochloric acid, and the lime precipitated as oxalate will give the total lime present, both caustic and as salts of organic acids; and by deducting the former, the weight of the latter may be obtained. If soda is present from the use of sulphide of sodium or soda ash in the limes, it may be first separated by washing the ignited and carbonated residue on a filter and titrating the solution with $N/10$ HCl and methyl orange. The insoluble calcium carbonate on the filter is then determined by dissolving in a known quantity of standard acid, and titrating back with methyl orange and HCl. From it must be deducted the amount found as caustic lime. Strictly, the

lime and alkalis should be calculated as oxides, and the corresponding amount of CO_2 added to the organic matter.

As it is not easy to keep a milk of lime so thoroughly mixed that equal quantities of the suspended lime can be pipetted off, it will generally be best to dilute with such a quantity of distilled water (free from CO_2) as will keep all the actual caustic lime in solution, as in the estimation of "available lime." Methyl orange is generally useless as an indicator in the case of lime-liquors, as it gives no sharp end-reaction from the presence of weak organic acids and bases.

Ammonia has an important influence on liming, swelling less, but dissolving more hide-substance than lime alone. Stiasny* has shown, however, that on mixture with lime, this effect is prevented, or greatly diminished, probably by the formation of complex lime-ammonia salts. It is usually present in greater or less quantity, being evolved from the hide-substance itself by the action of lime. It is best determined either by Procter and McCandlish's method (p. 60) or, preferably, by distillation (p. 63). In the latter case it must be borne in mind that old lime liquors are apt to froth excessively in boiling. Care is necessary in drawing samples, to take them from the freshly plunged lime, and to avoid loss of ammonia. Samples should be analysed without delay, as ammonia may be evolved from the organic matter present.

Amines (substituted ammonias) are contained in most lime liquors, and are less alkaline but otherwise similar in their effects to ammonia itself. By the distillation-method they will be mostly determined with the ammonia, but as they are less volatile, will probably be little estimated by Schloessing's process. Amido-acids are also present, but no convenient method is known for their determination.†

Alkaline Sulphides or sulphydrates derived from the addition of sodium or arsenic sulphide to the limes may be estimated by the zinc method given on p. 55. Not much is known either of their chemical action on the hair, or of what becomes of them in the process, but they usually disappear somewhat rapidly. Further investigation is very desirable. Arsenic may be detected by the Marsh test; for estimation see p. 58, remembering the presence of traces of organic phosphorus.

* Gerber, 1906, xxxii., pp. 200 *et seq.*; abstract Collég. 1907, p. 126. This paper contains much valuable information on the theory of the liming process.

† See, however, p. 90.

Dissolved organic matter of various sorts is always present. The substances of the hide are first peptonised and rendered soluble by the action of the lime, ammonia, and putrid ferments, and are gradually broken down to simple forms, such as amido-acids and amines. The total nitrogen of the liquor is easily estimated by the Kjeldahl method (p. 64), and from this the amount of dissolved hide-substance can be inferred; though it must not be forgotten that the epidermis matter, which it is the function of the lime to dissolve, as well as that portion of the cementing matter which it is desired to remove, are nitrogenous substances similar to the actual hide-fibre, and will, of course, be also estimated by Kjeldahling. A suitable quantity of the liquor to be examined, proportioned to its content of organic matter, should be pipetted into the Kjeldahling flask and acidified with sulphuric acid, and evaporated, nearly to dryness, before adding the concentrated acid for the actual digestion. Ammonia, if present, will of course be estimated with other nitrogenous matters. The amount of nitrogen found in analysis of really old limes, will not fully represent the total of nitrogenous matter dissolved, as considerable portions may escape in the form of ammonia from open lime-pits. All results are best stated as grms. per liter.

The Proximate Analysis of the various nitrogenous matters found in old limes is exceedingly complicated, and only possible to a certain extent, but for the tanner is only of minor importance, as he does not attempt to utilise or separate the dissolved matter, and even if, with our present knowledge, a proximate analysis could be made, it would not enable us to distinguish what portion of the products was derived from epidermis matters, and what from the fibre of the hide itself.

Eitner* has determined the organic substances in limes in the following manner. A measured quantity of the filtered lime liquor was first treated with carbon dioxide to precipitate the lime as carbonate, the liquor was warmed to drive off excess, and the precipitate collected on a tared filter, washed first with a little water, and then with slight excess of dilute hydrochloric acid to remove lime, again with water, and finally dried at 100° C., and weighed as "dissolved hide-substance in combination with lime."

The filtrate was then slightly acidified with hydrochloric acid and the further precipitate collected, washed and weighed as before, and reckoned as "organic substance uncombined with lime." This distinction strikes the writer as very doubtful, as it is by no means probable that all organic compounds of lime would be decomposed by carbonic acid.

The peptones were determined in the filtrate, either by an unpublished method of Eitner's, in which sodium hypochlorite is used as a precipitant, and which is founded on that of Jolles,* or by that of Hallopeau.† In the latter, the neutral or slightly acid solution is mixed with its own volume of a mercuric nitrate solution, and allowed to stand 18-24 hours. The precipitate is then collected on a tared filter, and washed with cold water till the wash-water is free from mercury, dried at 106°-108° C., and two-thirds of its weight reckoned as "peptones." The mercuric solution is prepared by heating 150 grm. of commercial pure mercuric nitrate with 1 liter of water for twenty minutes. After filtration the solution is heated nearly to boiling, and a solution of sodium carbonate is added drop by drop, with constant stirring, till a slight permanent precipitate is produced, when it is again filtered for use.

The total organic matter as determined by these methods comes out decidedly lower than the loss on ignition, and certainly does not include all the organic products present, and especially the amines and amido-acids.

The earlier products of the action of lime and ferments on gelatinous matter (peptones), though soluble in cold water, are still capable of being precipitated by tannin, and it may sometimes be of interest to determine what proportion of these matters, which are still capable of forming leather, or at least of acting as "fillings," have been washed out by any given mode of treatment, such as drumming or stocking. For this purpose the solution containing them may be rendered faintly acid with acetic acid, and precipitated with excess of tannin, and the precipitate filtered off and Kjeldahled. To facilitate filtration any non-nitrogenous substance, such as asbestos, kaolin, or paper-pulp may be added, or the filter paper itself may be placed in

* Zeit. Anal. Ch., 1890, xxix., p. 406.

† Compt. Rend., 1892, cxv. p. 356. Cp. also Ch. Zeit., 1892, No. 73, p. 263; *ibid.* No. 16, p. 263; *ibid.* 1893, No. 4, p. 42.

the digesting flask. If the quantity of organic matter added is considerable, it will increase the time required for digestion to a colourless solution, and a blank test with a similar quantity of the organic matter should be made to ascertain the absence of nitrogen, or to allow for it if present.

Probably a better method for the proximate analysis of gelatin and its decomposition products (peptones, amido-acids and amines) than any of the above, is that used by Wood and Trotman* in their examination of "Collin" (p. 233). The unchanged gelatin was precipitated by saturating its solution with zinc sulphate, and filtered off, and after washing with zinc sulphate solution, the wet precipitate was Kjeldahled, and the gelatin calculated. On the average of many analyses gelatin contains 18 per cent. of N. The clear filtrate containing zinc sulphate was treated with excess of bromine to precipitate peptones, and the bromine precipitate was similarly Kjeldahled, the nitrogen representing peptones, which have a lower percentage of nitrogen than gelatin or hide fibre. Finally, the nitrogen present in the filtrate represents the soluble lower compounds of nitrogen, such as amido-acids and amines. These methods may also be applied to the examination of glues and glue sizes.†

Bacteria and the enzymes or soluble ferments which they produce in their action on the skin play a large, if not the most important part in the unhairing process, and a hide may be fully limed, say by the Payne and Pullman process‡ without the hair being loosened, so long as bacterial action is excluded. Unfortunately few chemists engaged in tanneries have either the training, time, or appliances to undertake bacteriological work, and leather manufacturers have not yet realised its cardinal importance, so that our knowledge is very limited. It is, however, well recognised by the practical tanner, that though bacterial action may be essential to satisfactory liming, the presence of unsuitable bacteria is one of the most fertile causes of damage at this stage. The simplest forms of bacteriological investigation are described at some length in Section XXVI., and though a little personal instruction is of great help, leather chemists should not be discouraged in attempting at least the most elementary operations, such as plate culture, which would

Journ. Soc. Ch. Ind. 1904, p. 1071.

† Trotman and Hackford, Journ. Soc. Ch. Ind. 1904, p. 1072.

‡ Principles of Leather Manufacture, p. 157.

form the first step to a more complete investigation. With regard to limes, plate-culture in Petri dishes (p. 445) with a slightly alkaline peptone-gelatine (p. 443) seems the appropriate method, and if the gelatine were made distinctly alkaline with lime-water, it would restrict the growths to those capable of development under conditions similar to those of the limes, and so lessen the danger of contamination with the many germs of other sorts always floating about in tannery air. Roll-cultures (p. 445) in bottles in an atmosphere of nitrogen (i. e. air from which oxygen and carbonic acid had been absorbed by an alkaline solution of pyrogallol) would afford a means of studying the anaerobic organisms which must be active in deep limes; and the mere counting of the colonies capable of liquefying gelatine would be of value, since it is not likely that bacteria incapable of doing this can produce much injury to hides or skins. Stab-cultures in test-tubes (p. 444) are also suitable for the study of anaerobic organisms. From plate-cultures, pure cultures of the different organisms can be made, and their individual action on hide-substance studied. As old limes contain large numbers of bacteria, it will generally be desirable to dilute the liquor considerably with sterilised water before inoculating the culture-medium.

The enzymes or soluble ferments are precipitated by addition of a large volume of absolute alcohol, and their activity is not destroyed by ether or chloroform, or by drying at a low temperature, but is restored by solution in water, so that in this way they may be separated and studied apart from the living bacteria; but, of course, many of the products of gelatine-decomposition such as peptones would be precipitated with them, and it would be difficult to make any estimate of their quantity apart from their fermentative action. They are all nitrogenous bodies of the nature of albumins.

The direct microscopic examination of lime-liquors is often interesting, and living bacteria may be recognised and some times identified by a $\frac{1}{8}$ -inch or often by a $\frac{1}{4}$ -inch objective though for their more detailed study a $\frac{1}{16}$ -inch homogeneous immersion is desirable (p. 396).

In the microscopic examination of old lime-liquors, spherica crystalline concretions of carbonate of lime will frequently be noted, similar to those sometimes found in urines, or, on a muc

larger scale, in the dolomite rocks near Sunderland. It is probable that such globular concretions are in all cases due to crystallisation from liquids highly charged with organic matter. These crystalline bodies have often a somewhat deceptive resemblance to fungoid spores or other organised cell-structures.

Puers, Bates.—"Puers" are fermenting infusions of dog-dung, "bates" of pigeon- or hen-dung, but similar names are frequently applied to artificial mixtures, such as "coal-tar bate," which are really chemical deliming agents, and, however useful, are different in their effect to the dung-baths. Some other preparations, such as "Erocin," may fairly be denominated artificial puers or bates, since like the natural ones, they owe their efficacy to bacterial action and products, and are really artificial culture-media, to which a suitable bacterial ferment is supplied.* The object of puering and bating is partly to remove lime, but to a still greater extent to complete the solution or breaking up of the epidermis structures, to remove a portion of the cementing matter, and to bring the fibres into a flat and unswollen condition.

In this case, even more than in the limes, bacterial investigation is of the first importance, and much that has been just said of the bacterial examination of limes applies here also. Both bates and puers, though not necessarily alkaline when first made, speedily become so, owing to the lime introduced by the skins, though of course to a much less degree than the limes themselves, and this should be considered in the preparation of either liquid or jelly culture-media. Boiled and filtered bate or puer liquors, with the addition of gelatine, and sometimes of peptones, glucose and other nourishing substances, often form suitable media.

Most of our knowledge of the chemistry of puering and bating is due to the researches of J. T. Wood.† He has shown that the puering effect is principally due to the joint action of bacterial enzymes and amine salts, neither of which alone produces the full effect of true puering. The presence of living bacteria is not essential, though in practice it is advantageous, if injurious organisms can be excluded; and, no doubt, the am-

* On the principles of puering and bating cp. Principles of Leather Manufacture, Chap. XIII.

† Journ. Soc. Ch. Ind., 1894, p. 218; 1895, p. 449; 1898, pp. 856, 1010; 1899, pp. 117, 990. A summary is given in Principles of Leather Manufacture, p. 170 et seq.

moniacal salts and amido-acids present among the decomposition products of skin take their part in the removal of lime. Erodin, the artificial puer introduced jointly by Wood and Drs. Popp and Becker, is a dry powder consisting of peptonised products of hide-substance, together with some phosphate of lime and other salts needed for the proper nutriment of bacteria, which are contained in a separate culture which is added to the erodin infusion shortly before use. The culture is a mixed one, containing principally two species of bacteria which are found to work most effectively together. Neither of them liquefies gelatine. For details of use, *Principles of Leather Manufacture*, p. 174, may be consulted.

But little can be done in the way of actual chemical control of puers or puer liquors, as the process is too complex and largely bacteriological. Enzymes may be separated with alcohol as mentioned on p. 91, but will be a mixture of various kinds with peptones and other products which cannot be separated. Amines may be liberated by excess of calcined magnesia, and distilled off together with the ammonia, and collected in dilute hydrochloric acid, but their separation could only be accomplished by fractional crystallisation, and even then not quantitatively. By evaporating the mixed chlorides to dryness repeatedly with additions of water to remove free acid, and finally drying at somewhat over 100° , the weight of mixed chlorides may be determined. If now the amines and ammonia are liberated by excess of normal NaOH, and driven off by boiling, the hydrochloric acid with which they were combined may be determined by titrating back with N/1 HCl, and thus the mean molecular weight of the bases may be found. The total nitrogen may be determined by Kjeldahling, as in limes, but if the object is to estimate the solution of hide-substance, the nitrogen present in the liquor before use must of course be determined and deducted. Fat is emulsified by puers and bates, and worked out mechanically by the subsequent treatment on the beam. It could no doubt be estimated in the liquid "scudded" out by acidification and shaking out with ether, which would probably be a more suitable solvent than petroleum-ether, as the fat, like wool-fat, must consist partially of liquid waxes.

Drenches.—Drenching consists in treatment of the skin with fermenting bran infusions which have generated lactic or acetic acid, and its principal object is to remove lime, to cleanse from

the putrid ferments of the puer, and to bring the skin into a faintly acid condition without material swelling. For details of the process the reader is referred to Principles of Leather Manufacture, p. 166. The theory of drenching has been very fully studied by Wood.* The principal bacteria are *B. furfuris* α and β (Wood), shown in Figs. 41 and 42, p. 436, though other acid-producing bacteria may be concerned. They are incapable of fermenting the starch of the bran directly, but can only do so after it is converted into glucose by the action of cerealin, an enzyme naturally present in bran.

Bacterial examination is principally limited to the detection of false ferments which may produce injury to the skins. As the drench is normally weakly acid, culture-media for the drench organisms themselves should always be faintly acid, and contain glucose as a nutritive substance, together with traces of phosphates. Pasteur's or Cohn's solutions (p. 442) are suitable. If, however, the object of the examination is to detect putrid ferments introduced from the puers or elsewhere, media suitable for these, of a slightly alkaline character and containing nitrogenous nourishment, may be used with advantage.

Chemical examination is directed in the first instance to the quantity of acid present, and afterwards to its character. The total acid is easily estimated in the drench liquor with N/10 alkali, or with baryta-water or lime-water, with phenolphthalein as indicator, and may be calculated either as acetic acid (eq. 60), or as lactic acid (eq. 90). The usual quantity of mixed acids varies between 1 and 2 grm. per liter. In an experimental drench which Wood examined, which had not been used for skins, he found 0.7205 grm. acetic acid, 0.0402 grm. butyric acid, and 0.0918 formic acid in the volatile portion, and 0.7907 grm. of lactic acid per liter, beside traces of trimethylamine. No other non-volatile acids were detected, but the drench liquor on long-continued boiling deposited calcium phosphate and a trace of calcium oxalate. The gases given off during fermentation consist mainly of hydrogen, with carbon dioxide and nitrogen.

Wood determined the acids as follows:—The volatile acids were estimated by adding to 3 liters of the drench liquor a sufficient weighed quantity of pure calcium carbonate (in this case 5 grm.) to render the liquid alkaline, and the mixture was concen-

* Journ. Soc. Ch. Ind., 1890, p. 27; 1893, p. 422; 1897, p. 510; Brit. Assoc. Rep., 1893, p. 723.

titrated in a distilling flask till the distillate was no longer alkaline. The traces of base which distilled over were identified as trimethylamide. 100 c.c. of $N/1$ HCl were required to neutralise the calcium carbonate employed. 50 c.c. of this were first added, rendering the mixture very faintly acid, and the remainder in successive portions of 10, 10, 10, and 20 c.c., a fraction being distilled off after each addition. Each fraction was then boiled with barium carbonate, the barium salts formed were filtered off, and the residual barium carbonate well washed, and the solutions with their respective washings were evaporated to dryness, dried at 130°C ., and the barium salts weighed when constant. The salts were now decomposed with strong sulphuric acid, ignited, and the residue of barium sulphate determined. This of course enabled the mean molecular weight of the acids of each fraction to be calculated, and assuming the two first to be mixtures of butyrate and acetate, and the two last of acetate and formate, it became easy to calculate the proportions of each.

The nature of the volatile acids in each of the fractions was determined qualitatively. A portion of fraction 1, heated with concentrated sulphuric acid and alcohol, gave the characteristic pineapple smell of ethyl butyrate. Fraction 2 heated with sulphuric acid gave a strong smell of acetic acid. After filtering off the BaSO_4 , the solution was carefully neutralised with ammonia, concentrated, and added to a solution of neutral ferric chloride, when it became dark-red, and finely divided basic ferric acetate came down on boiling. Formic acid was detected by adding silver nitrate, and slightly acidifying the solution with acetic acid, when a little silver was deposited in the form of a metallic film.

To determine the non-volatile acids, four liters of the drench were concentrated to one liter, and filtered, the insoluble matters were well washed and the washings added to the filtrate, which was placed in a distilling flask and distilled with additions of water (of which four liters were required), until the distillate was no longer acid. During this operation the liquid again deposited solid matter, which had to be filtered off a second time and washed as before. 10 c.c. of the concentrated solution were repeatedly titrated with $N/10$ NaOH, using glazed litmus paper as an indicator, and, calculated to the original volume as lactic acid, gave 0.7481 grm. per liter of the drench. The presence of lactic acid was qualitatively established by heating 10 c.c. of the liquid in

a small distilling flask with 2 c.c. of concentrated sulphuric acid; and 1 gram. of potassium chromate. The distillate smelt of aldehyde and gave the usual reaction with magenta decolourised with SO_2 (see p. 80). This reaction is found by Wood to be a very delicate one for lactic acid, and is not given by succinic, malic, citric, or tartaric acids, nor by those of the acetic series. Succinic and malic acids were tested for, and found to be absent. In order to isolate the lactic acid, 100 c.c. of the concentrated liquid were decolourised with 10 gram. of animal charcoal, the mixture filtered, and the charcoal well washed, and the filtrate and washings evaporated to dryness. 15 drops of $\text{N}/10 \text{ H}_2\text{SO}_4$ were added to decompose lactates, and the residue was extracted with ether, which was distilled off and the acid converted into calcium lactate. The quantity of lactic acid found in this way was slightly larger than that found by direct titration, owing no doubt to the decomposition of the lactates. The particulars of this research have been given in some detail, as they contain useful suggestions for future work, and give some idea of the thoroughness and care of Mr. Wood's researches, but for the ordinary purposes of works-control it would no doubt be sufficient to estimate the total acid by direct titration of the drench liquor; and the volatile acids by distillation to small bulk, repeating the distillation with small additions of water, so long as the distillate contains perceptible traces of acid. Titration with lime-water and phenolphthalein is convenient, and if the lime water be standardised against 10 c.c. $\text{N}/1 \text{ HCl}$, which is equivalent to 60 mgr. of acetic or 90 mgr. of lactic acid, the calculation becomes one of simple rule-of-three.

While there is no doubt that the principal effect of the bran-drench is due to the organic acids produced by bacterial fermentation, it has been noticed that a mere unfermented infusion is not without action in removing lime, and a part of its effect has been attributed by Mr. E. M. Payne in conversation with the author to the presence of a peculiar organo-phosphoric acid, which has been shown by Patten and Hart* to exist in bran in combination with magnesium and small quantities of other bases, and which is probably identical with the anhydro-oxymethylene-diphosphoric acid extracted by Posternak† from beans and other seeds, to

* Bull. 250 New York Ag. Exp. Station; Ch. News, 1904, p. 112.

† Revue Générale de Botanique, 1900, xii. pp. 5 and 65. Compt. Rend., cxxxvii. Nos. 3, 5, 8.

which he gives the formula $O \begin{pmatrix} CH_2-O.PO(OH)_2 \\ CH_2-O.PO(OH)_2 \end{pmatrix}$. The free acid is a thick syrupy liquid, soluble in water. Its alkali salts are also soluble, those of magnesia and lime less so, and those of barium and strontium very sparingly. The magnesium and calcium salts are soluble in acetic acid. It exists in bran to the extent of about 2.75 per cent. It is somewhat analogous to the glycerophosphoric acid obtained by mixing glycerin and metaphosphoric acid, and if further investigation proves that it is of importance in the drenching process, it would be worth experimenting with the glycerin compound as a substitute.

Many substitutes have been proposed for bran-drenching, usually containing glucose, sugar, or other vegetable matters brought into fermentation, often with little knowledge of the proper fermentation to be produced. Weak glucose solutions with a little mineral nutriment like Cohn's solution (p. 442) set with the milk-ferment give good results, and could probably take the place of bran fermentation with profit in many cases. If fresh milk be set with a little sour milk, and the process repeated from day to day, an almost pure culture of the milk-lactic bacterium results, as no other organism thrives so well under the conditions. The method has long been used in producing a "starter" in souring milk for butter-making. The true drench bacteria are probably originally derived from the puers and cannot long be kept in a state of activity as a separate culture, without fresh nourishment, though in the drenching process they are sufficiently abundant about the vessels used to secure a continuance of the fermentation without intentionally added ferment.

Acids, both mineral and organic, have now in many yards largely taken the place of drenches, and even of puers, as a means of deliming, or to complete and shorten the fermentative process, which is always more or less dangerous to the goods. Lactic, acetic and formic acids in particular are very complete substitutes for drenching. Hydrochloric, and even sulphuric acids are successfully used even on light skins, for reducing the lime to a small residue, the process being usually completed by drenching or the use of organic acids. These stronger acids can also be employed to liberate the weaker organic acids or boric acid from the lime salts formed, and so economise the quantity

required in strengthening for successive parcels of skins. The acid effect of all organic acids is lessened by the presence of their own neutral salts in the solution, and the swelling power of mineral acids may be controlled by additions of salt; while organic salts added to solutions of mineral acids act as regulators of their action, liberating organic acids as soon as the mineral acid is in excess. For further details 'Principles of Leather Manufacture,' pp. 154 *et seq.*, may be consulted.

It is obvious that in all these cases accurate determination of the acids, both in the original solution and after use, is of great importance, but the ordinary alkalimetric methods will mostly suffice, methyl orange being usually the appropriate indicator for the mineral acids, and phenolphthalein with caustic standard solutions or with lime and baryta water for the organic. It is not easy to devise simple methods for the separate estimation of organic and mineral acids in mixture, though in some cases the different sensitiveness of indicators can be taken advantage of. If mineral acids are used to decompose the salts of organic acids it is usually well to be sure that the salts are in liberal excess. Boric acid may be estimated in presence of mineral acids by the methods given on p. 76, but very accurate results are not generally to be expected, since the organic acids from the skins usually affect the sharpness of the change of colour of methyl orange. The total boric acid can of course be accurately estimated by adding excess of base, and destroying the organic matter by ignition.

Control of Hides and Skins.—Beside the control of the liquors it is very important to adopt scientific methods in the examination of the hides and skins themselves during the preparatory processes, and especially, the tanner constantly wants to ascertain at the earliest moment the actual weight of dry leather-forming matter in his raw material, and consequently, the maximum weight of leather which he can expect to obtain. Attempts have frequently been made to calculate this from the weight of the soaked or limed pelts, but though these figures are useful guides in regular work, they are very variable, owing to the different moisture, amount of hair, and so on, in hides from the soaks, and the variability of the swelling in limed hides. Actual drying and weighing of portions of hide-material itself is impracticable both from the length of time which it occupies, and

the impossibility of getting really average samples. By far the best method is that of the determination of weight in water, a method probably first suggested by the writer to his students, but afterwards worked out in more detail by Carini,* and tested on a large scale by C. E. Parker and G. H. Russell.† In principle, this depends on the fact that water weighed in water weighs nothing, and that consequently the water-weight of a hide is simply that of the actual dry hide matter, less that of the water actually displaced by the dry matter itself. If a thoroughly soaked sponge be hung in water by a fine wire, from a delicate spring balance, it will be found to weigh exactly the same, whether squeezed out or allowed to expand; and in the same way, the swelling or flatness of the hide makes no difference to its water-weight unless indeed the actual density of the hide-substance is altered by some chemical change.

Parker and Russell prefer to weigh the hide or skin by attaching it by a thin copper wire to a delicate spring balance (Salter, Birmingham), or, with still greater accuracy, to a beam balance made for a similar purpose by Reimann, of Berlin. As the water-weight is only about $1/16$ of that in air, a delicate balance must be used, and care taken not to let the weight come upon it till the hide is really immersed in the water, and it must be hung in a deep pit or vessel in such a way that it does not inclose any air in its folds, and does not touch the sides of the pit. From the water-weight, the weight of dry matter is obtained simply by multiplication by a factor C, and deduction of the dry weight so found from the weight weighed wet in air gives the amount of water contained in the hides as weighed. The factor C will probably prove to be a constant when accurately ascertained for pure hide-substance, or at least to vary within very small limits. It may be determined either directly by dividing the water-weight of an average sample of hide by its actual dry substance as found by drying at 100°C ., weighing, and deducting any lime or other mineral substances present (remembering that the lime must be calculated as CaO , and not as carbonate), or the sample may be Kjeldahled, and the dry substance calculated from the nitrogen found, which would bring it into harmony with the hide-substance as determined in the

* Lancashire Tanners' Federation Year Book, 1905, p. 45.

† Collegium, 1905, pp. 161, 171.

leather by the same method. The factor C may also be determined by calculation from the specific gravity S of hide-substance, if the latter is known, as $C = S / (S - 1)$. On the whole, the first method is to be preferred as more direct, as it is not certain that the specific gravity of the swollen hide is exactly that of the hide dried at 100°C . If the gravity is taken direct, great care should be taken, especially in the more porous sorts of hide material, that no air is contained in the pores. This will probably be best attained either by actually weighing in water after placing the pycnometer for some time under an air-pump receiver to remove air, or by weighing in paraffin oil after prolonged soaking. Gravity can, of course, be calculated from the factor C , since $1 / (C - 1) = (S - 1)$. The presence of fat and other foreign matters, such as hair on the hide, will of course introduce errors, but these in most cases will be of small importance. The gravities are supposed to be taken at 15°C . or 60°F ., but small differences of temperature are quite negligible; a temperature of 25°C . only introducing an error of about 0.2 per cent. which is much less than probable errors of weighing. The influence of lime contained in the lime-water absorbed by the hide is somewhat greater, but will be allowed for in the factor, if this is determined experimentally under the same conditions. As in any case, rather relative than absolute results are required, the exact accuracy of the factor is not of much importance, so long as the same is always adhered to. Parker and Russell give the gravity of hide-substance in plumped butts as 1.425, which gives a factor C of $= 3.353$, and in plumped shoulders and bellies as 1.374, giving $C = 3.674$. They themselves, however, calculate the factors as $C = 3.38$ and 3.754 respectively. They quote the following from Carini as the result of many determinations of pelt dried at 100°C .

Hides ex soaks with hair on	$C = 3.216$	Sp. gr. = 1.45.
„ „ limes, unhaired	$C = 3.353$	Sp. gr. = 1.425.
„ unhaired with sodium sulphide	$C = 3.227$	Sp. gr. = 1.441.

Parker and Russell remark on the importance of the degree of swelling as influencing the tannage; and in this they are undoubtedly right, not only as regards sole-leather, but probably to a still larger degree in the case of skins and dressing goods, in which it is well known that the more the swelling is reduced,

the softer is the leather. As a measure of swelling they calculate what they call the "apparent specific volume" as (air-weight - water-weight) / (dry hide-substance). This figure does not seem to represent any actual physical quantity, but is apparently founded on a misconception, and it is surely better either to calculate the total wet weight of one part of dry substance, which is done by dividing the actual wet weight by the calculated dry substance, or the quantity of water held by one part of dry substance, which is of course one less than the above, since both of these figures are obvious actual quantities.

There is no need that this method of determining hide-substance should be confined to limed hides, as it is probably equally applicable in any stage of the wet-work, and should give valuable results as to the effect of bating, puering and drenching in reducing swelling. It is also applicable with some modifications to leather in process of tanning.

Lime in Hides.—The presence of caustic lime in hides is easily detected by moistening a freshly cut edge with solution of phenolphthalein, which will turn red or pink according to the quantity of lime present. Caustic soda or sodium sulphide gives a similar reaction. This test is extremely useful in judging of the extent of deliming by bates or drenches. The quantitative determination of caustic lime in the hide is somewhat difficult and troublesome, but is best done by a method devised by Mr. E. M. Payne. The hide or skin is cut into thin shavings, avoiding exposure to air as much as possible, and is weighed into a stoppered bottle with distilled water free from CO_2 and some phenolphthalein. N/10 HCl from a burette is now added till the red colour of the liquid is just discharged, and the bottle shaken and allowed to stand, when the liquid will again be reddened by lime diffusing from the hide. Further additions of acid are made very slowly and over many hours, till the red colour seen in the shavings just disappears, and the total acid used is calculated into caustic lime.

Total lime is determined by drying and igniting the sample, dissolving in excess of N/1 or N/10 HCl (according to the quantity of hide taken), and titrating back with standard caustic soda and phenolphthalein, or, if it be desired to include sulphate or chloride, by precipitation as oxalate (see p. 45). Payne *

* Lancashire Tanners' Year Book, 1905, p. 75; Collegium, 1905, p. 184.

gives the following percentages of lime calculated as calcium hydrate in hide dried at 100° C.

	Per cent.
Hide fully limed	3.766
Hide bated	0.689
Calf limed	2.601
„ bated	0.122
Goat limed	5.613
„ „	5.778
„ bated	1.268

The differences are very striking, and show the need of further investigation.

Acid in Hides and Skins.—If skins have been delimed or swollen with acid, it is sometimes desired to determine the excess which they contain. Total acid may of course be estimated by reversing Payne's process for caustic lime (*vide supra*) and titrating with caustic alkali or lime-water till a faint permanent red appears. Another and less tedious method is to place the weighed portion of hide in a bottle with distilled water, and a weighed portion of freshly ignited magnesia, and allow it to stand with occasional shaking till the acid is completely neutralised, which with thick hide may take many hours. The point of neutralisation may be determined by testing a freshly cut surface with litmus paper. The hide is carefully freed from adhering magnesia, and the whole of the undissolved MgO is collected on a filter, ignited and weighed, when the loss may be calculated into total acid. Probably methods could also be devised taking advantage of the fact that borax or sodium bicarbonate does not swell hide, but can be titrated as alkali in presence of methyl orange. Free mineral acids may be estimated in presence of their salts (as in pickled skins) by adding excess of N/1 NaCO₃ to a weighed portion, evaporating the whole to dryness, igniting gently, extracting the ash with water, and then completing the ignition, finally adding the extracted solution, evaporating to dryness, and again gently igniting, and titrating back the soda solution, when the loss will represent mineral acids. The error to be guarded against is the reduction of sulphates by the organic matter, and their subsequent conversion into carbonates. For this reason the salts are as far as possible removed from the organic matter by washing, either before drying or after very gentle ignition. The use of most oxidising agents would be

inadmissible, as they would produce variations in the alkalinity of the residue. (Compare p. 369 on the estimation of free acids in leather.) The loss of sodium chloride is of no consequence as it is a neutral salt, and calcium or magnesium chlorides which are dissociated on ignition cannot exist in the material after treatment with sodium carbonate.

SECTION VIII.

THE CHEMISTRY OF TANNINS AND THEIR DERIVATIVES.

THE essential constituents of tanning materials are various members of a large group of organic compounds called tannins, or tannic acids,* which are widely distributed throughout the vegetable kingdom, and which are said to occur in one insect, the corn weevil. Their function in vegetable physiology is yet uncertain, and in some cases they appear to be waste products of organic changes.

These bodies often differ widely both in chemical constitution and reaction, but have the common property of precipitating gelatin from solution,† and forming insoluble compounds with gelatin-yielding tissues. By virtue of this power, they convert animal hide into the insoluble and imputrescible material called "leather."• They are mostly uncrystallisable; and all form blackish-blue or blackish-green compounds with ferric salts, and, in common with many other organic substances, are precipitated by lead and copper acetates, stannous chloride and many other metallic salts. In some cases the tannin combines with the base only, liberating the acid; but frequently the salt as a whole enters into combination. This is the case with the precipitates formed with lead and copper acetates. Tannins are also

* Ger. *Gerbsäure*; in German, the word *Tannin* denotes usually gallotannic acid only.

† Certain bodies have been described as tannins, such as "moringatannic acid," or maclurin, and "caffetannic" and "lupulotannic" acids, which do not precipitate gelatin or tan hide, and, in the writer's opinion, are more closely related to the colouring matters than the tannins.

precipitated by many organic bases, such as quinine, morphia, and most of the basic colouring matters. With alkalis, the tannins and many of their derivatives give compounds which oxidise and darken rapidly, usually becoming successively orange, brown, and black. A. H. Allen has shown that these bodies also give instantaneously a deep-red coloration with a solution of potassium ferricyanide and ammonia. The reaction is one of considerable delicacy.

Tannins are more or less soluble in water and glycerin; and freely so in ethyl and methyl alcohol, mixtures of alcohol and ether, acetone and ethyl acetate, but scarcely in dry ether alone, nor in dilute sulphuric acid; and insoluble in carbon disulphide, petroleum spirit, benzene and chloroform.

A. G. Perkin* points out that the colouring matters of plants usually yield the same decomposition products as the tannins associated with them, though this is not invariably the case. The following table shows this in a convenient form:—

Tanning Material.	Tannin Contained.	Decomposition Products of the Tannin.	Colouring Matter.	Decomposition Products of the Colouring Matter.
Quebracho colorado	Quebrachotannin	Phloroglucol † and Protocatechuic acid	Fisetin.	Resorcinol. Protocatechuic acid.
Rhus species	Gallotannin	Gallic acid	Myricetin	Phloroglucol. Gallic acid.
Catechus	Catechin	Phloroglucol and Protocatechuic acid	Quercetin	Phloroglucol. Protocatechuic acid.
Cape Sumach	A catechotannin	Protocatechuic acid.	Quercetin	Phloroglucol and Protocatechuic acid.
Divi-divi	Ellagitannin	—	Ellagic acid	—

The natural tannins are all compounds of carbon, hydrogen and oxygen only. They all contain the benzene group of carbon atoms, but their ultimate structure is, except in the case of gallotannic acid, very imperfectly understood, and probably differs considerably in type in different members of the family. They may be regarded as derivatives of the phenols

* Dr. Nierenstein (Collegium, 1905, p. 69) shows that Quebracho also contains tannin which yields resorcinol.

† Journ. Chem. Soc. 1898, pp. 374, 665, 1016.

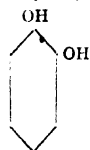
(hydroxybenzenes) and their corresponding acids, of which a general view is given in the following table :—

C_6H_6 Benzene.	C_6H_5OH Phenol.	$C_6H_4(OH)_2$ Catechol (1 : 2). Quinol (1 : 4). Resorcinol (1 : 3).	$C_6H_3(OH)_3$ Pyrogallol (1 : 2 : 3). Phloroglucol (1 : 3 : 5). Hydroxyquinol (1 : 2 : 4).
$C_6H_5CO.OH$ Benzoic acid.	$C_6H_4(OH)CO.OH$ Salicylic acid (1 : 2). 2 Oxybenzoic acids, Meta- (1 : 3). Para- (1 : 4).	$C_6H_3(OH)_2CO.OH$ Protocatechuic acid (and 5 other isomeric acids).	$C_6H_2(OH)_3CO.OH$ Gallic acid (3 : 4 : 5). Pyrogallolcarboxylic acid (2 : 3 : 4). Phloroglucolcarboxylic acid (2 : 4 : 6). 3 possible acids unknown.

The figures in brackets represent the relative position of the OH groups round the benzene ring. In the acids the CO.OH group counts as No. 1.

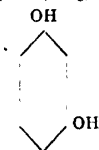
It will be noticed that a large proportion of the formulae given above represent several isomeric compounds, identical in composition, but frequently very distinct in their properties. The explanation of these differences lies in the different relative positions of the OH and CO.OH groups round the benzene ring. Thus the following diagram represents the probable relative positions of the dihydroxybenzenes.

(Ortho-, 1 : 2).



Catechol.

(Meta-, 1 : 3).



Resorcinol.

(Para-, 1 : 4).



Quinol.

Besides these six-carbon phenols, others exist in which one or more of the H-atoms are substituted by methyl or higher hydrocarbon groups, as in the case of ordinary alcohols. Thus the cresols are $C_6H_4(CH_3)OH$, and yield acids (cresotinic),

* The dihydroxybenzenes yield six possible isomeric acids, two from ortho-, three from meta-, and one from para-dioxybenzene, all of which are known.

analogous to salicylic, which have been used as antiseptics and chemical bates. The OH groups may also be replaced by methoxyl, OCH_3 , ethoxyl, OC_2H_5 , and other similar compounds. As these higher phenols may enter into the constitution of tannins, it will be seen that the possibilities of complication are very great. Vanillic and isovanillic acids are the meta- and para-methylprotocatechuic acids.

Miller,* who has investigated these acids, remarks: "Of the three phenols $\text{C}_6\text{H}_4(\text{OH})_2$, catechol alone gives a precipitate with lead acetate, and of the six acids, $\text{C}_6\text{H}_3(\text{OH})_2\text{CO} \cdot \text{OH}$, none yield precipitates with lead acetate except the two which are derived from catechol.

Researches by Berthollet and Werner† on the heat evolved by neutralisation with soda throw some light on the constitution of these polyhydric phenols. Resorcinol and quinol yielded about double the heat given by ordinary phenol, showing that both their OH groups have a similar function to that of phenol. Catechol, on the other hand, in which the groups occupy the ortho-position, gave only the same heat as phenol, showing that only one of its OH groups behaves like that of a phenol, while the second has apparently alcoholic functions. In pyrogallol and phloroglucol, two OH groups have phenolic and one an alcoholic function. The authors suggested that pyrogallol has its OH groups in the 1 : 2 : 3 position, phloroglucol in the 1 : 2 : 4, leaving the 1 : 3 : 5 for the third isomeric phenol, not then discovered. Later work has shown that phloroglucol has the 1 : 3 : 5 position. Researches by A. Lambert‡ have shown that polyhydric alcohols having a primary alcoholic function, as glycerol, levulose and dextrose, combine with boric acid to form energetic conjugated acids much stronger than boric acid itself. (See p. 75.) This reaction is given by pyrogallol, catechol and alkaline gallates and tannates, but not by quinol or resorcinol.

All natural tannins, when heated to $180^\circ\text{--}200^\circ\text{C}$., yield either catechol or pyrogallol or both, together with secondary products and frequently phloroglucol, and may be conveniently classified as catechol and pyrogallol derivatives, as the two groups are marked by considerable difference of character. Artificial pro-

* Journ. Chem. Soc. xli, 1882, p. 399.

† Compt. Rend., c., p. 586; Chem. Soc. Abst., 1885, p. 628.

‡ Op. cit., cviii., p. 1017; Chem. Soc. Abst., 1889, p. 864.

ducts, having many of the reactions of tannins, have, however, been obtained from other phenols, and most phenols and their derived acids give purplish or greenish blacks with ferric salts.

Several classifications of the tannins have been suggested. The division most obvious to the tanner is between those tannins which yield ellagic acid as a whitish deposit in the surface of the leather, called "bloom," and those which do not. Stenhouse, many years since, divided tannins into two classes, one of which gives bluish, and the other greenish blacks with ferric salts. In the main, both these classifications correspond to that just suggested, as most tannins which yield a blue-black with iron acetate also give bloom to the leather, and the green-black is generally characteristic of catechol derivatives, and the blue-black of those of pyrogallol. In some cases, however, the difference of tint is due to accidental impurities, or the presence of colouring matters, and is largely dependent on the acid or alkaline condition of the solution, since even gallotannic acid will give a decided green with strongly acid ferric chloride. The Australian mimosas generally give a dull violet with iron salts, though they unquestionably belong to the catechol class. Pure gallotannic acid yields no bloom, because it contains no ellagic acid, though it is of course the representative pyrogallol derivative, while ellagic acid, though closely related to gallic acid, yields no pyrogallol on heating, and belongs rather to the colouring matters (p. 140) than the tannins, though it is a decomposition product of ellagitannic acid.

A reaction, which appears to be quite universal with catechol tannins, is that when their dilute solutions are treated with excess of bromine water, insoluble bromine derivatives are produced which cause turbidity or precipitates, while with pyrogallol tannins only soluble derivatives are formed and the solution remains clear. This was first pointed out by the present writer in a paper read before the International Congress of Chemists held at Chicago in 1893.* Nicrenstein† has shown that catechol tannins give a precipitate with a dilute solution of diazobenzene chloride (an insoluble azo-compound), while pyrogallol tannins do not. Catechol tannins usually form crimson solutions in concentrated sulphuric acid, while pyrogallol tannins give brown or yellow.

Journ. Soc. Ch. Ind., 1894, p. 488.

† Collegium, 1906, p. 376.

Trimble points out * that the tannins may be divided into two groups, one of which contains about 52 per cent. of carbon, and the other about 60 per cent. The first of these includes gallotannic acid, and the allied tannins of sumach, chestnut and pomegranate, all of which are known to be pyrogallol tannins; and the second the catechol tannins, among which must be reckoned cutch, gambier, oak bark, mangrove, canaigre, etc. A few of the analyses cited by Trimble are given below.

GROUP I.—PYROGALLOL TANNINS.

	Carbon.	Hydrogen.	Oxygen.
Sumach tannin (Löwe)	52.42	3.56	
Chestnut tannin (Nass)	52.07	3.97	
Chestnut bark tannin	52.42	4.67	
Chestnut wood tannin	52.11	4.40	
Pomegranate bark tannin (Culley)	50.49	3.99	
Gallotannic acid, $C_{11}H_{12}O_9$	52.10	3.52	44.38

GROUP II.—CATECHOL TANNINS.

	Carbon.	Hydrogen.	Oxygen.
Oak bark tannin (avg. 9 species)	59.79	5.08	
Oak bark tannin (Htti)	59.29	4.99	
White oak bark tannin (Kraemer)	59.65	4.65	
Mangrove tannin	59.76	4.60	
Canaigre tannin	58.10	5.33	
Rhatany tannin (Ohmeyer)	59.20	4.72	
Kino tannin (Bergholz)	59.65	4.87	
Catechu tannin (Lowe)	61.93	4.80	
Tormentil tannin (Rembold)	60.75	4.65	

If tannins are boiled with dilute sulphuric or hydrochloric acids, or allowed to ferment under the influence of pectose and other natural ferments which are usually present in vegetable tanning materials, a different series of decompositions takes place. Many tannins yield glucose, or starch sugar, as one of

* 'The Tannins' ii p. 121.

their products, or as that of closely associated impurities; of which more must be said later. In addition it will be found that the catechol tannins invariably yield insoluble reddish-brown bodies, which have been called phlobaphenes or "reds," and which seem often derived from the original tannins by loss of one or more molecules of water, or, in other words, are anhydrides of their respective tannic acids. The pyrogallol tannins, on the other hand, yield gallic acid, or ellagic acid (the deposit forming bloom), either alone or in mixture. It is possible that the so-called "ellagitannic acid" is merely a soluble glucoside of ellagic acid, which exists ready formed in the plant, though it is more probably a gallic acid derivative. Oak bark and valonia give both bloom and insoluble reds, as well as traces of gallic acid. It is quite possible that this is due to their containing a mixture of catechol and pyrogallol tannins.

If the red anhydrides, which are produced from the catechol tannins, or the tannins themselves, or their lead-salts, be fused with caustic potash, or in many cases, if simply boiled with concentrated potash solution, they are broken up still further, and from the fused mass, protocatechuic acid (which bears the same relation to catechol that gallic acid does to pyrogallol) may always be obtained. This is in many cases accompanied by phloroglucol. Cutch, gambier, mimosa, quebracho, and many other materials contain phloroglucide tannins. The tannins which do not yield phloroglucol frequently give acetic acid and other acids of the acetic series, along with protocatechuic acid, and sometimes other products. The presence of phloroglucol may often be detected without the necessity of a potash-fusion by the reaction with deal shaving described on p. 152. If, however, more than one of its hydroxyls are substituted or linked to other groups, it does not react in the compound, though it may be found among the products of decomposition.

The classification of tannins is as yet very incomplete, and there are many of which the decomposition products have not been examined. In order to make the information available for further research, the characteristics and mode of recognition of the different products will be given, and as simple a scheme as possible of treatment of the tannin to be examined will be described; but the recognition of such products in a state of mixture presents great practical difficulties, and the tanner will usually

be compelled to confine his attention to simpler, though less conclusive tests, based on the colour-reactions of the unpurified infusions of tanning materials. Such tests will be described later (p. 149 *et seq.*).

Preparation and Purification of Tannins.—The great obstacle to successful investigation of the tannins is the impossibility of preparing them in a state of actual purity, as none of them can be crystallised or volatilised, so that the use of appropriate solvents, and fractional precipitation are almost the only means at our disposal. A further difficulty lies in their very unstable character, and in many cases it is impossible to be sure that the supposed purified tannin is really identical with the original substance, and not merely a product of its decomposition.

When, as is frequently the case, two or more tannins occur in the same plant, it is often quite impossible completely to separate them. Owing to their considerable differences in character, no general method of purification can be given, but the following processes will be found in many cases to give good results. For the special methods adopted by different investigators, the original memoirs must be consulted, references to many of which will be found in the following pages.

The oldest method of separating tannins from other constituents is that applied by Pelouze to the preparation of commercial gallotannic acid from gall-nuts. The finely pulverised material is placed in a percolator and exhausted with commercial ether containing water and alcohol. The liquid separates, on standing, into two layers, of which the lower contains most of the tannin in a tolerably pure form, dissolved in water and alcohol with a little ether, while the upper mainly ethereal layer contains the gallic acid. Gall-nuts thus treated yield 35 to 40 per cent. of tannin. If equal parts of ether and 90 per cent. alcohol are used, a larger yield is obtained, but the liquid does not separate into two layers, and it is questionable if the product is so pure. For Chinese galls, washed ether acts better than ether-alcohol. The tannin may be still further purified by dissolving in a mixture of 1 part water with 2 of ether, when three layers are formed, of which the lowest contains nearly pure tannin. Commercial ether generally contains a considerable percentage of alcohol.

These methods are applicable to the dried or highly con-

centrated extracts of many tanning materials. Many tannins may be separated from their strong aqueous solution in a state of considerable purity by first agitating with ether to remove gallic acid, and then saturating the aqueous solution with common salt, and shaking with acetic ether, which takes up the tannin. The acetic ether is distilled off nearly to dryness, and the last traces expelled by drying on the water-bath with small repeated additions of ether, which expels the acetic ether and leaves the tannin in a porous mass. Another method is to extract with alcohol, evaporate to a small bulk at as low a temperature as possible, and treat at once with a considerable quantity of cold water to precipitate phlobaphenes which are filtered off. The infusion is then precipitated with successive small quantities of lead acetate; the first and last portions of the precipitate are rejected as contaminated with colouring matters and other impurities, while the middle fraction, after rapid washing, is suspended in water and decomposed with sulphuretted hydrogen. The solution is filtered, and the excess of SH_2 driven off by heat, and the aqueous portion is either evaporated at a low temperature in a partial vacuum to a thin syrup, and the drying completed over sulphuric acid in vacuo; or, preferably, shaken out with acetic ether. Dr. Nierenstein and the author have observed that in many cases treatment with SH_2 appears to decompose or alter the tannin, and prefer to liberate it with a quantity of dilute sulphuric acid insufficient to decompose the whole of the lead salt. Compare also Schiff.

Prof. Trimble* has made use of acetone as a solvent for the extraction of tannins with great advantage. The following is the general method he adopted in his researches on the oak tannins. The powdered bark was covered with acetone in a percolator and allowed to macerate for 48 hours. It was then percolated somewhat rapidly till 500 c.c. of percolate per kilogram of bark was obtained, which was mostly sufficient for exhaustion; the acetone retained in the bark was displaced by water, and the acetone recovered from the percolate by distillation on the water-bath, the last portions being removed under reduced pressure. The dry residue was dissolved in a small quantity of warm water, or of alcohol sp. gr. 0.975, filtered and then diluted with water so long as anhydrides and colouring

* 'The Tannins,' ii. p. 75. Philadelphia, 1894.

matter were precipitated. The solution was again filtered, and shaken out with successive portions of acetic ether. The acetic ether solution was distilled off under reduced pressure, and the tannin further purified by solution in water and shaking out with acetic ether. The acetic ether was finally removed by solution in ether-alcohol, which was distilled off under reduced pressure, and the dry tannin digested with absolute ether to remove traces of resin and other impurities. The resultant tannins were pale coloured and perfectly soluble in water. In the case of common oak bark (*Q. robur*) it was necessary to add salt before shaking with acetic ether, and in some cases the lead method of purification was employed.

It is not always necessary to separate the tannin itself in a state of purity, since much light can be thrown on its constitution by investigation of its metallic salts or organic products. The lead salts have been used both for ultimate analysis, and for fusion with potash, and some experiments have been made in the author's laboratory in investigating the insoluble bromine-derivatives of the catechol tannins, which are obtained in a state of tolerable purity by precipitation of the dilute solutions with bromine-water. Some insoluble diazo-compounds have also been prepared, but without much result.

GENERAL METHODS OF EXAMINATION OF TANNINS.

Decomposition by Heat.—The ordinary method is to distil the tannin or dried extract in a small retort, and examine the distillate for catechol and pyrogallol. Unless the heat be very carefully regulated, much loss is caused by the destruction of the catechol and pyrogallol with formation of metagallic acid, etc., and their detection is greatly complicated by the presence of secondary products. This difficulty is somewhat lessened by passing a stream of carbon dioxide through the retort, which carries the products quickly out of the heated portion. A better method is to heat the tannin in glycerin.* About 1 gram. of the sample is heated with 5 c.c. of pure glycerin to 160° C., and the temperature slowly raised to 200°–210° C., at which it is maintained for twenty or thirty minutes. After

cooling about 20 c.c. of water is added, and the liquid is shaken with an equal volume of ether, without previous filtration. As the ether when shaken with the glycerin is apt to form a troublesome emulsion, Trimble* recommends shaking the glycerin solution with 20 c.c. of ether without previous dilution with water; or heating the dry tannin in 5 grm. of paraffin, which is removed with petroleum ether and the residue taken up with water and treated as above. The ethereal layer, which may contain pyrogallol and catechol, and possibly phloroglucol or other phenols (cp. p. 109), is separated from the aqueous portion, evaporated to dryness, and dissolved in 50 c.c. of water. The filtered solution is divided into several portions and tested by the table on p. 118. By these means it is easy to distinguish between catechol and pyrogallol, and either may be detected in presence of a small portion of the other; but if in nearly equal quantities their recognition is difficult. Catechol may be derived from catechin, etc., and pyrogallol from gallic acid, and it is therefore necessary in some cases to remove these bodies from the tannin before treatment by shaking its aqueous solution with ether. Phloroglucol is produced from all the colouring matters of the flavone group (p. 141) on fusion with potash (except fisetin which yields resorcin), and in most cases together with protocatechuic acid; and these colouring matters are frequently associated with the tannins, usually as glucosides. As a general rule, however, catechins and catechol derivatives are only present in any quantity with catechol tannins, and the same is true of gallic acid with regard to pyrogallol.

Products of the Decomposition of Tannins by Heat.

Pyrogallol, $C_6H_3(OH)_3$ (formerly called pyrogallic acid, but really a phenol), has a bitter, but not sour taste, and feebly reddens litmus; the addition of the smallest trace of alkali gives it an alkaline reaction. It is somewhat poisonous, but less so than some other phenols. It is soluble in less than three parts of cold water, and still more freely in hot. It is also soluble in alcohol, ether, acetone, ethyl acetate and glycerin, but not in absolute chloroform or petroleum spirit. It fuses at $132^\circ C.$ out of toluol, but ordinarily at $115^\circ C.$, and sublimes at about $210^\circ C.$

* 'The Tannins,' i. p. 27.

With pure ferrous sulphate it gives a white precipitate, which redissolves to a fine blue liquid in presence of the least trace of ferric salt. Mineral acids change this to red, and the blue tint is restored by cautious neutralisation with ammonia, and is not destroyed, but sometimes rendered greenish, by excess of acetic and other organic acids. Any excess of ammonia produces an amethyst-red, and acetic acid restores the blue. Ferric chloride and other acid ferric salts produce a red coloration at once. Pyrogallol solution is turned brown by traces of nitrous acid. With lime-water it produces a beautiful but evanescent purple, rapidly turning brown. In presence of alkalies it absorbs oxygen from the air with great avidity, turning orange, brown, and black; and is therefore used as an oxygen-absorbent in gas analysis. Pyrogallol does not precipitate gelatin. Its solution rapidly reduces permanganate, Fehling's solution, and salts of gold, silver,* mercury and platinum. It precipitates copper and lead acetates, and with ammoniacal cupric sulphate it gives an intense purple brown coloration, and, in common with gallic and gallotannic acids, is coloured purple-red by iodine in either aqueous or alcoholic solutions. Gum arabic, saliva, and various other organic matters cause solutions of pyrogallol exposed to the air to absorb oxygen, forming purpurogallin, which separates in small yellow or orange-red needles. If 0.2 per cent. of pyrogallol be added to a 1 per cent. solution of gum arabic, it becomes yellow in a few hours, and purpurogallin separates in hair-like crystals, which continue to increase for some months. If these crystals are freed from pyrogallol by washing with water, and a trace of alkali is added, they dissolve in absence of oxygen to an orange-red solution, which rapidly oxidises to an intense blue colour, and finally to a brownish yellow. Purpurogallin is also formed by oxidation with silver nitrate, potash permanganate and ferricyanide, nitrous acid, and many other reagents. Potassium nitrite, and probably nitrous acid is also capable of producing purpurogallin from gallic acid, and it is very possible that the colour-reaction of pyrogallol-tannins described on p. 162 may be due to its formation. A. G. Perkin and Stevens,† and A. G. Perkin and F. M. Perkin,‡ have lately investigated and described

* Hence its use as a "developer" in photography.

† Journ. Chem. Soc., 1903, lxxxiii. p. 194.

‡ Op. cit., 1904, lxxxv. p. 243.

this substance very fully, and have devised a method of preparing it in considerable quantities by electrolytic oxidation of pyrogallol. It appears to be a naphthalene derivative. Pyrogallol forms compounds with aldehydes; with formaldehyde, a body which reacts like a tannin and precipitates gelatin is produced. If pyrogallol be heated with hydrochloric acid and aldehyde, chloral or acetone, a red substance is produced. The less volatile portions of crude beech-tar creasote contain ethers of pyrogallol, methyl-pyrogallol and propyl-pyrogallol, and of the corresponding catechol derivatives, from which these bodies may be obtained by the action of hydrochloric acid under pressure. The methyl and propyl derivatives differ from the original phenols in having one or more atoms of hydrogen replaced by the groups CH_3 or C_3H_7 respectively; and it is very possible that some tannins are derived from them. Tribrom- and trichlor-pyrogallols are formed by the action of bromine or chlorine on pyrogallol.

If pyrogallol be heated rapidly to 250°C . it parts with the elements of water, and is converted into metagallic acid, $\text{C}_6\text{H}_4\text{O}_3$, a black amorphous body, insoluble in water, soluble in alkalis. When pyrogallol is made in the ordinary way, by heating gallic or tannic acid to 210°C ., much metagallic acid is formed, even if the process be conducted in a stream of carbonic acid, and the yield of pyrogallol usually amounts to only about 5 per cent. of the gallic acid employed (see p. 120).

On boiling pyrogallol with hydric potassic carbonate, pyrogallo-carboxylic acid is produced, which only differs from gallic acid in the position of its CO.OH group (p. 119), and like it is resolved into pyrogallol and CO_2 on heating.

Phloroglucol (Phloroglucin), $1:3:5 \text{ C}_6\text{H}_4\text{O}_3$, is a trihydric phenol, isomeric with pyrogallol. It crystallises with two molecules of water, which it loses at 100°C . It melts at about 220°C ., sublimes without odour, and solidifies again on cooling. It is soluble in water, alcohol, and ether, and by agitation with the latter it may be removed from its aqueous solution. It is not precipitated by any metallic salt but basic lead acetate. When pure it gives no reaction with ferric salts. If bromine be added to its concentrated solution in water, it absorbs three atoms, forming tribromophloroglucol, $\text{C}_6\text{Br}_3(\text{OH})_3$, which separates in crystalline needles, with evolution of heat and a very irritating

odour. In dilute solution it gives a bulky white precipitate with bromine water. If deal shaving be moistened with solution of phloroglucol, and then with strong hydrochloric acid, it soon takes a deep violet colour, from the formation of phloroglucol-vanillein with the trace of vanillin contained in all coniferous woods. Neither catechol nor pyrogallol gives this reaction when free from phloroglucol; though Etti has stated that pyrogallol forms a somewhat similar bluish compound when mixed with vanillin and hydrochloric acid. Resorcinol gives a similar reaction but of a much bluer shade, but this may be due to the presence of phloroglucol as an impurity. Nierenstein, however, obtained the reaction from resorcinol, purified with extreme care.* This reaction may be used to detect phloroglucide tannins without the troublesome fusion with potash, and is strongly given by gambier and cutch, and more faintly by many other tanning materials (see pp. 157-167, *et seq.*). Many colouring matters, however, such as quercetin (p. 142), and possibly some tannins, yield phloroglucol on fusion with potash, but contain the phloroglucol nucleus in such a form that it does not react with vanillin. For the reasons given, the results must be accepted with some reserve. If to a dilute solution of phloroglucol a solution of aniline or toluidine nitrate be added, and then a trace of potassic nitrite, the liquid gradually becomes yellow or orange, then turbid, and finally deposits a cinnabar-red precipitate. This reaction is given by many tanning materials, but is somewhat unsatisfactory, as gall tannin, pyrogallol and other substances give similar but browner precipitates.

Phloroglucol is more commonly obtained by fusion with potash than by direct heating, but as it may occur in the products of dry distillation, it is described here, together with the other polyhydric phenols.

Catechol (Pyrocatechin), $1 : 2 \text{ C}_6\text{H}_4(\text{OH})_2$, is not only produced by the decomposition of certain tannins by heat (see p. 113), but by the dry distillation of protocatechuic and $1 : 3 : 4$ dioxybenzoic acids, and of catechin and some colouring matters which contain the catechol groups, and which frequently accompany the tannins. It is also formed together with pyrogallol and its homologues (see above) by the dry distillation of wood, wood-tar, creasote consisting largely of ethers of catechol and its homologues

* Collegium, 1906, p. 14.

methyl- and propyl-catechol, etc., and is hence found in crude pyroligneous acid, and causes the greenish-black colour of "iron-liquor." It has also been produced by long continued heating of starch, cellulose and other carbohydrates with water under pressure, and is found ready formed in Virginia-creeper (*Ampelopsis hederacea*), and probably in other plants. It has also been formed synthetically by fusion of the 1:2 chlor- and brom-phenols, and by fusion of 1:2 benzenedisulphuric and phenol-sulphuric acids with potash.

Catechol melts at 104°C. , and sublimes at about the same temperature, condensing in brilliant laminae like benzoic acid. Its actual boiling point is 245°C. (Richter). It is readily soluble in water, alcohol and ether, and is extracted from its aqueous solution when shaken with the latter. Its aqueous solution precipitates lead acetate, by which it is distinguished from resorcinol and quinol. It does not precipitate gelatin or alkaloids. Its slightly alkaline solution exposed to air becomes first green, then blue and black. With excess of lime-water or caustic soda solution it becomes reddish, but remains clear for some time. It does not colour ferrous salts, but gives a dark green with ferric (avoiding excess) and after some time a black precipitate. The green is changed to a fine violet-red by alkalies and hydric sodic carbonate, and restored by acids. It has been stated that it gives a violet coloration to fir wood moistened with hydrochloric acid, but this is due to contamination with phloroglucol, and is not given by pure catechol. Catechol gives a red coloration with citric acid, and the solution, after standing, ceases to react with iron. Like pyrogallol, it reduces silver salts in the cold, and has been used as a developer in photography. Alkaline copper solutions (Fehling's solution) are only reduced by the aid of heat.

Resorcinol (Resorcin), $1:3 \text{ C}_6\text{H}_4(\text{OH})_2$, though not common as a constituent of tannins, is stated by Dr. Nierenstein to be present in quebracho tannin, together with quinol (p. 104), and it is quite possible, therefore, that both may be present in other tannins. It melts at 118°C. , volatilises at a somewhat higher temperature, and boils at 276°C. (Richter). It is easily soluble in water, alcohol, and ether, and may be removed from its aqueous solution by shaking with the latter. It is known to be a product of the dry distillation of brazil-wood extract. It is obtained synthetically

from the meta- (1 : 3) benzene and phenol compounds in the same way as catechol from the ortho- (1 : 2) derivatives. Commercially it is prepared from meta-benzenedisulphuric acid, and is important in the preparation of many artificial colouring matters. Lacmoid, used as an indicator, is produced by heating resorcinol with sodium nitrite; resazurin by the action of nitrous acid on its ethereal solution. It is possible that one or other of these reactions might be used as a means of identification. Resazurin crystallises in lustrous green prisms and dissolves in alkalis to a violet solution with brown fluorescence. Resorcinol is not precipitated by lead acetate.

Quinol (Hydroquinone), 1 : 4 $C_6H_4(OH)_2$, melting point $169^\circ C.$, soluble in water, alcohol, and ether. It is precipitated by lead acetate in presence of ammonia only. It reduces silver in alkaline solution, and is used as a photographic developer. It has two crystalline forms, subliming in monoclinic scales, and crystallising from solutions in hexagonal prisms.

DISTINCTION BETWEEN PYROGALLOL, CATECHOL AND PHLOROGLUCOL.
1 PER CENT. SOLUTIONS.

Reagent.	Pyrogallol.	Catechol.	Phloroglucol
Ferric alum	Blue-black, turning green and brown.	Dark green.	No reaction.
Lime-water	Violet coloration, rapidly turning brown.	No marked reaction.	No marked reaction.
Deal shaving and HCl	No colour.	No colour.	Violet-red coloration
Bromine-water ..	No precipitate.	No precipitate.	Bulky white precipitate.

Decomposition of Tannins by Dilute Acids.—It has been stated that tannins, when heated with dilute sulphuric or hydrochloric acids, are decomposed, yielding either gallic or ellagic acids or red anhydrides, and frequently glucose. To determine whether glucose is produced, the tannin must first be carefully purified from glucose, gums or other bodies likely to interfere, by the methods mentioned on p. 110. Either the tannin itself or its washed lead-salt may be used, and must be heated to $100^\circ C.$ for an hour or more in a sealed tube or tightly closed bottle

or boiled in a flask with reflux condenser, with dilute hydrochloric acid (2 per cent. HCl). Complete decomposition is, however, somewhat difficult. After cooling, the mixture must be allowed to stand for some time to separate any sparingly soluble products, which must be filtered off. The filtrate must be shaken with ether to remove gallic acid, etc. (p. 120), the aqueous solution must be boiled, neutralised with sodic hydrate, precipitated with basic lead acetate to remove any traces of tannin or colouring matters, the liquid again filtered, and excess of lead removed with dilute sulphuric acid, excess of acid and all elevation of temperature being carefully avoided. The mixture is neutralised with sodic hydrate, and the clear filtrate heated to boiling, with Fehling's copper solution, when a red precipitate of cuprous oxide proves the formation of glucose. (Cp. also p. 270.)

The precipitate separating from the hydrochloric acid solution on cooling may consist of lead chloride, if the lead salt has been used, of ellagic acid, or of insoluble red anhydrides or phlobaphenes of the tannin. The lead chloride may be removed by washing with boiling water; and the phlobaphenes by cold alcohol, which leaves them on evaporation, or on dilution with water. If the remaining precipitate has a pale yellow or fawn colour it probably consists of ellagic acid (see p. 121), which may be crystallised from hot alcohol or pyridine. It is soluble in ammonia and reprecipitated by acids, and dissolves freely in strong nitric acid, forming a crimson or deep yellow liquid.

The ethereal solution which contains the gallic acid, if any has been formed, must be evaporated to dryness, and the residue taken up with cold water and filtered. Addition of a few drops of solution of potassium cyanide will produce a fine red coloration if gallic acid be present, which rapidly fades, but is restored by shaking in presence of air. The sodium arsenate test is also a delicate one. For this and other reactions of gallic acid see p. 120.

Products of the Decomposition of Tannins by Acids.

Gallic Acid (Trihydroxybenzoic Acid), 1 : 3 : 4 : 5 $C_6H_2(OH)_3CO.OH$, exists ready formed in some plants, and is a product of the hydrolysis of gallo-tannic acid under the influence of the unorganised ferment pectase, or of its decomposition by boiling with acids or alkalis. It crystallises in white or yellowish-white

needles, containing 1 mol. (9·5 per cent.) of water, which it loses at 100° C. It is soluble in 100 parts of cold, or 3 of boiling water, in alcohol or glycerin, and slightly so in ether, by agitation with which it may, however, be removed from its aqueous solution. Gallic acid fuses at a temperature of about 232° C.,* but at about 210° C. begins to lose carbon dioxide, and yields a crystalline sublimate of pyrogallol (see p. 113). If the heat be raised suddenly to 250° C., a considerable quantity of black shining metagallic acid is formed.

When gallic acid is heated with concentrated sulphuric acid to 140° C. dark red rufigallic acid is formed, and is precipitated on dilution with water. Rufigallic acid is a hexaoxyanthraquinone related to alizarine. It forms a blue solution with alkalis, and dyes brown on chrome mordants. A. J. Perkin † has employed this reaction as a means of identifying gallic acid, and it is strongly recommended for this purpose by Nierenstein.

Aqueous solution of gallic acid gives the following reactions:—Solution of ferric chloride gives a deep blue coloration which is destroyed by boiling. Ferrous sulphate, if free from ferric salts, gives no reaction in dilute solutions, but a white precipitate in strong ones. The mixture rapidly darkens by oxidation. In alkaline solution gallic acid absorbs oxygen from the air and darkens from the formation of galloflavin, and afterwards of tannomelanic acid. Lime-water produces a white precipitate which rapidly becomes blue from oxidation (distinction from pyrogallol). The same reaction is produced by baryta-water, or by the chlorides of barium or calcium on addition of ammonia. Gallic acid is distinguished from gallotannic acid by the following:—It does not precipitate gelatin, except in the presence of gum. It does not precipitate tartar emetic in presence of ammoniac chloride, though both tannin and gallic acid are precipitated by tartar emetic alone. It precipitates lead acetate, but not lead nitrate, while tannin precipitates both. A dilute solution of potassium cyanide gives a red coloration which disappears on standing, but is restored by shaking with air. If to even a very dilute solution of gallic acid, sodic arsenate, or some other faintly alkaline salts be added, the mixture absorbs oxygen and becomes a deep green. Aqueous solution of picric acid to

* Etti, Chem. Soc. Abst., 1879, p. 160.

† Proc. Chem. Soc., 1896, p. 157.

which excess of ammonia has previously been added gives a red coloration, changing to green. Tannic and pyrogallie acids produce no reaction with cyanide, and with ammonium picrate a reddish coloration only. Gallic acid reduces silver nitrate and gold chloride rapidly when hot, but not Fehling's solution, and decolorises acidified potassic permanganate. If tannin and other oxidisable bodies be removed from its solution, it may be estimated quantitatively by titration with permanganate in presence of indigo (see p. 224). Tannin may be separated from it by gelatin or hide power (see pp. 208, 224) but much gallic acid is also absorbed. Gallotannic and quercitannic acids may also be removed by precipitation with ammoniacal solution of cupric sulphate, or by cupric acetate, in presence of excess of ammoniac carbonate (see also p. 171). Many other tannins, however, give precipitates with cupric salts which are soluble in ammonia and ammoniac carbonate.

Gallotannic acid may also be separated from gallic acid by lead acetate strongly acidified with acetic acid, by which tannic acid is precipitated, while lead gallate is dissolved; and by many organic bases, such as cinchonidine, brucine, morphia, and many of the basic colouring matters; but none of these separations are very satisfactory. Strychnine, however, precipitates gallotannic acid quantitatively (see p. 169).

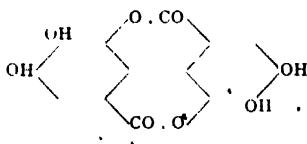
Ellagic Acid $C_{14}H_6O_8$, is a decomposition product of ellagitannic acid (p. 109), and may be obtained from the tanning materials which contain this tannin. It is deposited from aqueous infusions of these as a yellowish white solid, known as "bloom." It may be prepared by pouring a hot concentrated alcoholic extract of divi-divi into water, when it separates, and may be filtered off and re-crystallised.

It may also be obtained by boiling divi-divi, myrobalans, pomegranate rind, etc., with dilute hydrochloric acid, and extracting the washed and dried insoluble residue with hot alcohol, from which it crystallises on cooling. Another convenient source of ellagic acid is the "Alizarine yellow in paste" of Messrs. Meister, Lucius and Brüning, which after drying may be readily purified by crystallisation from pyridine. Lowc* was the first to prepare ellagic acid synthetically by oxidising gallic acid with arsenic acid, and this was subsequently accomplished by Ernst

and Zwenger* by heating the acid ethyl gallate with sodium carbonate solution in the presence of air, and by Griessmeyer† by heating gallic acid with water and iodine. The best method, however, for its synthetical preparation is one due to A. G. Perkin,‡ who oxidises a 10 per cent. solution of gallic acid in acetic acid with potassium persulphate and a little sulphuric acid. When the reaction is complete, the mixture is poured into water, and the resulting sandy precipitate is collected, washed, dried, and purified by crystallising from boiling pyridine, in which it dissolves somewhat readily. The prismatic needles eventually obtained are a pyridine salt of ellagic acid, most of the pyridine being removed by washing with alcohol and the final traces by drying at 160° C.

Thus obtained, it forms a crystalline powder, melting above 360° C., soluble in dilute caustic alkaline solutions with a pale yellow colour. It is itself very pale yellow, and is almost insoluble even in boiling water, and only slightly so in cold alcohol and ether, though by agitation with the latter, small quantities may be completely removed from aqueous solution. In hot alcohol, it dissolves with a yellow colour and crystallises on cooling. Solid ellagic acid gives with ferric chloride at first a greenish, and then a black coloration. With nitric acid containing nitrous acid, and subsequent dilution, it gives a deep crimson coloration (Griessmeyer's reaction), though that obtained from some natural sources is rather orange.

A constitutional formula was first suggested by Schiff,§ afterwards by Graebe,|| and it was finally proved by A. G. Perkin¶ to be a double lactone of a hexa-hydroxydiphenyl dicarboxylic acid. The formula is as follows:—



It will be noticed that the formula is symmetrical, and the formation by the oxidation of gallic acid is readily understood.

Annalen, 1871, cliv. p. 32.

Journ. Chem. Soc., 1905, lxxvii. p. 1412.

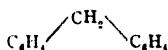
Ber., 1903, xxxvi. 212.

† Annalen, 1871, cliv. p. 55.

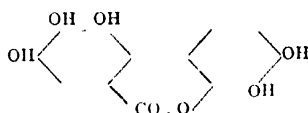
§ Ber., 1879, xii. 1534.

¶ Journ. Chem. Soc., 1905, lxxvii. 1412.

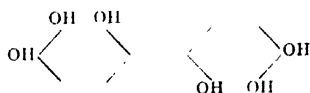
It forms a tetra-acetyl compound (m.p. 343–346° C.) and a tetra-benzoyl compound (m.p. 332–333° C.), and on distillation with zinc dust yields fluorene



On boiling with concentrated caustic potash, one lactone group is opened, and the carboxyl group eliminated, yielding on neutralisation and dilution pentahydroxydiphenylmethylolid.



This compound melts above 300° C., and yields penta-acetyl and penta-benzoyl derivatives, and fluorene on distillation with zinc dust. On fusing ellagic acid with alkalis, the reaction is carried a stage further, and the other lactone group similarly attacked, the final product being hexa-hydroxydiphenyl.



When heated at 230° C. with 100 per cent. sulphuric acid, ellagic acid is oxidised to form a new compound* $\text{C}_{14}\text{H}_8\text{O}_{10}$, which crystallises from pyridine and is soluble in strong alkalis with a greenish yellow tint changing to blue on dilution. This compound gives a hexa-acetyl derivative. Flavellagic acid also yields this compound.

Ellagic acid is a feeble colouring matter, dyeing yellows with tin and alumina mordants, and various duller shades with chromium and iron mordants.*

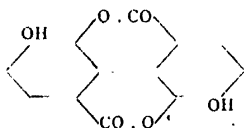
Catellagic Acid $\text{C}_{14}\text{H}_8\text{O}_8$ was obtained by Schiff† on heating protocatechuic acid with arsenic acid, and recently by Perkin,‡ by the oxidation of protocatechuic acid in sulphuric acid solution with potassium persulphate, and was purified by crystallisation

Proc. Chem. Soc., xxii. 308, p. 114. † Ber., 1882, xv. p. 2590.

‡ Journ. Chem. Soc., 1905, lxxxvii. p. 1418.

in pyridine as with ellagic acid, which it very strongly resembles in its properties.

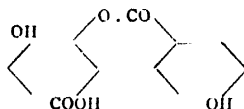
It is a pale yellow crystalline powder, melting above 360°C ., subliming much more readily at higher temperatures than ellagic acid. It dissolves in concentrated nitric acid, forming a magenta coloured liquid, which on standing changes to a dull brown, and from which on dilution with water, a yellow crystalline precipitate, probably a nitro-compound, is deposited. Caustic alkalis dissolve it with a pale yellow colour, which is discharged on warming. Its constitution is as follows :—



A diacetyl derivative is easily prepared (m.p. $322-324^{\circ}\text{C}$.), and fluorene obtained on distillation with zinc dust. It does not dye mordanted calico.

Catellagic acid is also formed by the persulphate oxidation of para-hydroxybenzoic acid in sulphuric acid solution, another hydroxyl group being first introduced forming protocatechuic acid, and the diphenyl condensation afterwards taking place.

Another compound is also formed in this reaction, by the diphenyl condensation of para-hydroxybenzoic acid and protocatechuic acid. It has the constitution :

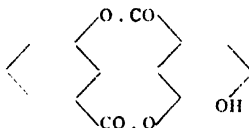


This compound does not melt below 360°C . and does not sublime. It is very readily soluble in pyridine, yields a diacetyl compound (m.p. $267-268^{\circ}\text{C}$.), and also fluorene on distillation with zinc dust. It dissolves with bicarbonates of sodium and potassium, and in hot potassium acetate, and forms salts. Nitric acid gradually attacks it, and yields an orange red liquid. It does not dye mordanted calico.

Metellagic acid $\text{C}_{14}\text{H}_6\text{O}_6$ was prepared by Perkin* by the

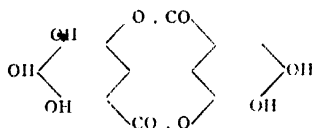
Journ. Chem. Soc., 1905, lxxvii. p. 1426.

persulphate oxidation of meta-hydroxybenzoic acid in sulphuric acid solution. It is isolated from the mixture of products so obtained by the repeated re-crystallisation of its acetyl derivative and subsequent hydrolysis. Its constitution is as follows:—



It resembles catellagic acid in that at high temperatures, it sublimes readily in the form of needles. It is soluble in pyridine and deposits long prismatic needles therefrom. Sulphuric acid dissolves it with a pale yellow colour, and nitric acid on gentle warming with an orange yellow tint, and on diluting this solution with water, a yellow precipitate, probably a nitro compound, is deposited. With caustic alkali solutions, it behaves like catellagic acid, and fluorene is obtained on distillation with zinc dust. It forms a crystalline mono-acetyl derivative, melting at $273-276^{\circ}\text{C.}$, and does not dye mordanted calico.

Flavellagic Acid (hydroxyellagic acid) $\text{C}_{14}\text{H}_8\text{O}_9$ was obtained by Perkin* by the persulphate oxidation of gallic acid in the presence of dilute sulphuric acid. If 96 per cent. sulphuric acid be used, ellagic acid is produced also. It is purified by crystallisation from pyridine, in which it is less soluble than ellagic acid. Its constitution is shown thus:—

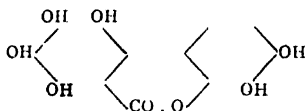


Small, pale yellow, prismatic needles are obtained from pyridine, which latter is removed, as with ellagic acid. The pure compound does not melt below 360°C. , and is insoluble in the usual solvents. It is more yellow than ellagic acid, and its solution in dilute alkalis has a well-marked green tint. It gives the Griessmeyer reaction with nitric acid, and fluorene by distillation with zinc dust. It dyes mordanted woollen cloth in shades resembling, but stronger than, those produced by ellagic

* Journ. Chem. Soc., 1906, lxxxix. p. 251.

acid. It yields a sparingly soluble penta-acetyl compound (m.p. 317° – 319° C., and a penta-benzoyl compound (m.p. 287° – 289° C.)

On boiling with 50 per cent. caustic potash, a reaction similar to that with ellagic acid occurs, one lactone group being opened, the carboxyl eliminated, and hexa-hydroxydiphenylmethylolid obtained.



This compound melts above 300° C., dissolves readily in pyridine, from which it cannot easily be crystallised. Caustic alkalis dissolve it with a dull orange-yellow tint, which on dilution and exposure to air, becomes bluish violet. Alcoholic lead acetate gives an orange-yellow precipitate which rapidly passes into olive green, and alcoholic ferric chloride a bluish green colour. Its solution in sulphuric acid is orange-yellow. Nitric acid dissolves it with an orange colour which becomes redder on dilution, but is devoid of the blood-red tint of the Griessmeyer reaction. It dyes mordanted calico and woollen cloth. The hexa-acetyl compound melts at 232 – 234° C., and the hexa-benzoyl compound at 261 – 263° C.

A somewhat full account of the ellagic group has been given (and perhaps out of proportion to its direct interest to the tanner), because, owing to the researches of Perkin, its constitution is now fully cleared up, and will probably serve as a starting point for further work elucidating the structure of the tannins themselves.

The *phlobaphenes* or *reds* are chemically the anhydrides of certain tannic acids from which they are derived, or in other words they are formed from the tannins by the loss of one or more molecules of water. It is in this way that they are produced by the action of acids; and similarly they are often formed when alcoholic or highly concentrated, aqueous extracts are poured into cold water, under which circumstances a part of the tannin seems unable to take up water again, and separates as a red precipitate. It is also possible that in some cases oxidation as well as dehydration takes place. Freezing also seems to have a dehydrating effect. Most solutions of catechol tannins are decomposed by long-continued boiling or heating

under pressure, with formation of reds ; which also exist ready formed in most tanning materials capable of producing them. They are soluble in alcohol, by which they may be extracted from tanning materials or dried residues containing them. They are also dissolved by dilute alkalis and alkaline carbonates and sulphites, and by borax, which is said to be used in the preparation of some extracts, and was tried by Sadlon as a means of rendering phlobaphenes available for tanning, but without much practical success. More successful results have been obtained by Lepetit Dollfus and Gansser's* process of heating with bisulphites under pressure, which give up base to the phlobaphenes, while the sulphurous acid prevents oxidation, and apparently to some extent combines with the tannins. Many phlobaphenes are scarcely soluble in water even at a boiling temperature, though they become more so in the presence of sugar, tannic acid, and some other substances. Their solubility in water depends on their degree of hydration, many tannins giving a series of anhydrides, of which those containing only one molecule of water less than the original tannin are quite soluble in water, while the higher members of the series become less and less soluble as they lose water. Those which are soluble form the principal colouring substances of tanning materials, and generally are practically tannins, precipitating gelatin and combining with hide to form leather. Hemlock bark yields a series of such bodies, of which the lower members are deep red soluble tannins, while the higher form the red sediment, so well known to extract-tanners. Thus it is chemically impossible to decolorise hemlock extract without at the same time greatly lessening its tanning power, though by careful manufacturing and concentration at low temperature, the proportion of the higher anhydrides formed may be kept at a minimum. In many cases it is known, as in gambier, and in others it is probable that the tannin itself is merely the first anhydride of the series, and derived from a catechin which itself is a white crystalline body destitute of tanning properties (see p. 137). The more soluble "reds" are identical with the so-called "difficultly soluble tannins."

Decomposition of the Phlobaphenes by Fusion with Caustic Alkalies.—It has been mentioned (p. 116) that the reds of different tannins yielded, in addition to protocathechuic acid, either phloro-

* E. P. No. 8582, 1896. Journ. Chem. Soc. Abstr., 1896, p. 436.

glucol, or acetic acid, or some other member of the fatty acid series, and some tannins, as those of alder and hop, give more than one of these, but it is possible that this may arise from the presence of two distinct tannins in these materials. It is stated that all those tannins which yield acetic acid on fusion with potash, also yield considerable quantities of glucose to dilute acids, while the phloroglucide tannins do not do so. It is stated by Barth and Schroder* that a small quantity of phloroglucol is produced by the fusion of gallic acid, resorcinol and common phenol with caustic soda. It is therefore possible that in some cases where phloroglucol is detected, it may have been formed by the action of the alkali, and not have been originally a constituent of the tannin. Note also its formation from the flavones (p. 141).

The following method may be employed to investigate the products of the action of potash. 20 grm. of the red, or of the tannin from which it is derived, or its lead salt, is boiled with 150 c.c. of solution of caustic potash of 1·20 sp. gr. for three hours, and the liquid is then concentrated with constant stirring till it becomes pasty. In many cases the tannin is sufficiently broken up by mere boiling with the potash solution, and occasionally products are obtained in this way which are broken up by actual fusion. The melt or solution is cooled and treated with a volume of dilute sulphuric acid slightly more than enough to neutralise the alkali employed. After further cooling it is filtered from potassium sulphate and other solid matters, and the filtrate treated with sodium bicarbonate till its wine-red reaction with litmus shows that the sulphuric acid is neutralised. The liquid is then shaken with an equal measure of ether, the ethereal layer drawn off, and the treatment repeated several times. On distilling off the ether, phloroglucol is left and may be purified by solution in water, when protocatechuic acid and other products may be precipitated by neutral lead acetate, and filtered off, and the phloroglucol again extracted with ether, and recognised by its reaction with deal-shaving and hydrochloric acid and by its sweet taste.† Other tests for phloroglucol have been already described on p. 118. It is quite possible that phloroglucol may exist in the tannin in some cases at least as

* Journ. Chem. Soc. Abst., 1883, p. 60.

† Compare Allen, Commercial Organic Analysis, iii., p. 86.

phloroglucol-carboxylic acid, which is isomeric with gallic acid, but is much less stable than protocatechuic acid, and would be broken up by fusion with potash. It has also been shown that in many organic colouring matters a benzene ring linked to other groups in the meta-position breaks up into phloroglucol on fusion, though it does not give the reaction with deal-shaving in its original combination (p. 113).

Protocatechuic Acid, 1 : 3 : 4 $C_6H_3(OH)_2CO \cdot OH$, one of the six isomeric dihydroxybenzoic acids of this formula (see p. 105), crystallises in needles and plates with one molecule of water, which it loses at $100^\circ C$. The water-free acid melts at $199^\circ C$, and is decomposed into catechol and carbonic acid. It is somewhat soluble in cold water, and readily so in hot water, alcohol, or ether. It is coloured bluish-green by ferric chloride and ferric alum, and the colour is changed first to blue and then to red by very dilute alkalis. Many other catechol derivatives react similarly.* Solutions of protocatechuates give a violet coloration with ferrous salts. It is precipitated by lead acetate, and reduces silver ammonio-nitrate, but not Fehling's solution. With bromine-water it gives soluble bromine-derivatives. Boiled with dilute arsenic acid, it forms di-protocatechuic acid, $C_{14}H_{10}O_7$ *, a tannin very similar in its properties to gallotannic (digallic) acid (p. 130), but giving green-blacks with ferric salts.

Protocatechuic acid is formed by fusion with potash of many tri-derivatives of benzene which have substituted groups in the 3 : 4 positions, and therefore does not necessarily exist ready formed in all bodies which yield it. Many colouring matters and resins also yield it on fusion with potash or soda.

* *Catechol-ortho-carboxylic Acid*, 1 : 2 : 3 $C_6H_3(OH)_2CO \cdot OH + 2OH$, is extremely similar to protocatechuic acid, and like it, yields catechol and CO_2 on heating to $199^\circ C$. It is formed synthetically, and is not known to occur in natural tannins.

Vanillic and Iso-vanillic Acids are derivatives of protocatechuic acid, in which a methoxyl group substitutes one hydroxyl, the three in vanillic, and the four in isovanillic acid. They may occur among the products of the fusion of tanning and colouring matters with potash. Vanillic acid melts and sublimes at $211^\circ C$; iso-vanillic at $250^\circ C$.

The *resorcylic acids* are acids of resorcinol isomeric with those

* Schiff, D. Chem. Ges. Ber., 1882, xv. p. 2589.

of catechol. Dr. Nierenstein states that resorcinol is one of the products of fusion of quebracho-tannin with potash.* Similar acids are also derived from quinol, and it is possible that both resorcinol and quinol tannins may exist.

CONSTITUTION OF TANNINS.

Having described the products of decomposition of tannins, something must be said of the way in which these constituents are combined. Our knowledge is, however, very limited on this subject, and cannot be said to be by any means certain, even on the constitution of gallotannic acid itself.

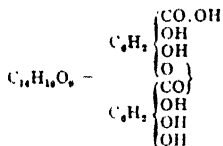
Gallotannic or Digallic Acid exists as the principal tannic acid of the galls of oak, tamarisk, etc. ; and, in mixture with more or less ellagitannic acid, in myrobalans, divi-divi, sumach, pomegranate rind, and many other plant-products. It probably exists in the plants originally as a glucoside, or at least as a carbohydrate compound which yields glucose and gallotannic acid on hydrolysis. It was first apparently synthesised by Löwe in 1867, by the action of argentic nitrate on barium gallate.† Schiff attempted a synthesis from gallic acid, in 1871,‡ by mixing the latter, after drying at 110° C., with phosphorus oxychloride to a thin paste, and heating, first to 100°C. and then to 120°C. Much hydrochloric acid was evolved and the gallic acid was converted into a yellow powder, which, after purification by washing with absolute ether, dissolving in water, allowing the gallic acid to crystallise out, saturating with salt, washing the precipitated tannin in salt solution, and redissolving in alcohol and ether, had all the reactions of gall tannin, but was perfectly reconverted into gallic acid on boiling with hydrochloric acid, without the formation of any trace of ellagic acid, or glucose. By analysis of the tannin and its acetyl compounds it appeared to be digallic acid, but the precise mode of condensation is yet very uncertain, and it is doubtful whether natural tannin is identical with the synthetic ; and doubts have recently been thrown on the reality of the synthesis.

* Collegium, 1905, p. 69.

† J. Prak. Ch., cii. p. 111.

‡ Ber. D. Ch. Ges., iv. p. 231.

Schiff suggested the following formula :—



B. Hunt * believed he had synthesised a tannin of this constitution by digesting potassium gallate and monobromprotocatechuic acid with alcohol on the water-bath for five hours, $\text{C}_6\text{H}_2(\text{OH})_3.\text{COOK} + \text{C}_6\text{H}_2\text{Br}(\text{OH})_2.\text{COOH} = \text{C}_6\text{H}_2(\text{OH})_3.\text{COO}.\text{C}_6\text{H}_2(\text{OH})_2.\text{COOH} + \text{KBr}$, but his results have not been confirmed on re-examination by Schiff,† who points out that monobromprotocatechuic acid itself precipitates gelatin, albumen, and quinine.

By boiling an aqueous solution of gallic acid with arsenic acid, which underwent no permanent change in the process, Schiff ‡ confirmed an earlier observation of Löwe's, and obtained a product which precipitated gelatin and otherwise reacted like tannin, which he regarded as digallic acid, but Freda § failed to obtain digallic acid by this means, and found that on complete removal of arsenic, the compound was reconverted to gallic acid. It was, therefore, questioned whether digallic acid was really formed, and reconverted into gallic acid by the prolonged action of hydric sulphide, which is necessary to remove the arsenic, or whether the supposed tannin was merely an arsenical compound of gallic acid. By shaking out with acetic ether, however, it has been stated that the digallic acid may be isolated free from arsenic; it has been noticed that the use of hydric sulphide in decomposing lead tannates (p. 111) often liberates a substance which has lost the characteristic power of precipitating gelatin. Small quantities of As_2O_3 will convert large quantities of gallic acid in time, but Schiff preferred to use 8–10 per cent. on the gallic acid. A minute quantity of As_2O_3 added to sumach liquors preserves and restores their tanning powers, and it was the active constituent of the writer's "Antigalline," sold some years ago for the purpose.

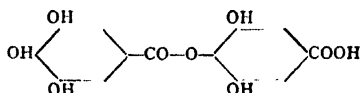
* Ch. News, lii. p. 49.

† Ch. Zeit., 1896, p. 866.

‡ Ann. Chem. Phar., clxx. p. 100.

§ Gaz. Ch. Ital., viii. pp. 9 and 363.

Vournasos* has recently repeated some of the earlier work on gallotannic acid, and prepared it free from gallic acid and other impurities by the repeated re-crystallisation and subsequent hydrolysis of what he considers to be a penta-acetyl derivative. He summarises and confirms the evidence for the view that gallotannin is a compound formed by the linking up of the carboxyl group of one molecule of gallic acid with a hydroxyl group of another molecule, water being eliminated, but points out that it has never been yet settled, which hydroxyl group is used to form the etheric grouping. He prepares a penta-benzoyl derivative of gallotannic acid, and describes its properties in detail, and uses this to clear up the constitutional formula. By the very careful action of sulphuric acid and alcohol on this compound, hydrolysis of the etheric linking between the two molecules of gallic acid is effected, without eliminating any of the benzoyl groups, and the product is separated into two portions, one of which is identified as tribenzoyl gallic acid, and the other as a dibenzoyl gallic acid. The latter in ethereal solution is treated with sodium amalgam at a low temperature, and the benzoyl chains substituted by hydrogen, thus yielding a hydroxybenzoic acid. This is identified as the 1:4 compound, and shows that gallotannin has the following constitution:



Vournasos also examines the supposed synthesis of Schiff by means of arsenic acid and phosphorus oxychloride, and finds with other observers, that the phosphorus and arsenic cannot be completely removed without destroying the "tannin," and he concludes that no real synthesis of a tannin has been yet brought about. The question of optical activity is not taken into consideration by him.

Gallotannic acid as obtained from plants invariably yields traces of glucose, as well as of ellagic acid, when boiled with dilute acids. It is still an open question in many cases whether the glucose exists in the plants as a glucoside of tannic acid or is the product of some impurity (as is shown by Etti to be the case

* Dr. Alexandre Vournasos, *Le Tannin de la Noix de Galle, Sa Constitution*.
Baillière et Fils, Paris, 1903.

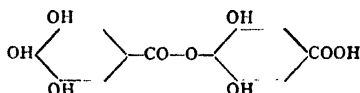
with oak bark, where lævulose is always present). It seems most probable, however, that natural gallotannic acid is really a glucoside of digallic acid, or possibly, according to the theory of Hlasiwetz, a gummiide, or compound of dextrin, which, by the action of acids, is easily converted into glucose. Schiff gives the formula $C_{34}H_{28}O_{22} = C_6H_{12}O_6 + 2C_{14}H_{10}O_8 - 2OH_2$, which corresponds to 23 per cent. of glucose, and slightly exceeds the maximum actually determined. He points out that natural gallotannic acid is freely soluble in ether-alcohol and absolute alcohol, which do not readily dissolve glucose. Repeated purification with ether-alcohol, however, is capable of removing most if not all the glucose from gallotannic acid. What has been said of gallotannic acid in this respect, applies to many other tannins, which like it give glucose by treatment with acids.

It has been recently pointed out by Günther,* that solutions of natural tannin are distinctly dextrorotary. The rotation is too large to be accounted for by any possible admixture of glucose or any other known substance. It is little altered by acetylation of the tannin, but disappears entirely on its conversion into gallic acid by digestion with dilute hydrochloric acid, which scarcely affects glucose. Schiff's synthetic digallic acid is optically inactive. It is generally believed that the property of rotating polarised light is due to the presence in a compound of an *asymmetrical* carbon atom, or one connected with four groups all of different character; and Günther remarks that this is not present in Schiff's formula given above. Schiff† confirms this, but shows that the power of rotation is very variable in different samples, and quite absent in gallic acid and artificial digallic acid (produced by treatment of gallic acid with arsenic acid). He suggests a ketonic formula, which, however, only contains an asymmetric carbon atom on the unproved benzene-theory of Claus, which supposes that the unsatisfied valencies are directed diagonally across the ring. In his second paper he shows that such a formula involves six hydroxyl groups capable of acetylation, while five only exist, and gives other reasons why such a ketonic structure is very improbable. On the whole, a suggestion made by A. G. Perkin in conversation with the writer seems to offer the most probable explanation, viz. that natural tannin consists of a grouping of two or more molecules of digallic acid, possibly

* Ber. Phar. Ges., 1895, v. p. 179.

† Ch. Zeit. 1895, p. 1680; 1896, p. 865.

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This constitution would readily account for the optical activity, the slow hydrolysis into gallic acid by acids, the absence of the carboxyl group, the formation of diphenylmethane on distillation with zinc dust, and the formation of rufigallic acid. The formula shows seven hydroxyl groups, one of which is supposed to be peculiarly situated,* so that only hexa-derivatives are obtained by the ordinary reagents.

The whole matter, however, is still in an unsatisfactory condition, and confirmatory work is urgently needed.

Phenols may be sulphonated by treatment with disulphuric (fuming sulphuric) acid, forming sulphonic acids, analogous to the carboxylic, but in which SO_3 takes the place of CO_2 . When these acids are treated with phosphorus oxychloride disulphonic acids are produced analogous to the synthetic tannins, and possessing very similar properties, precipitating gelatin, and producing more or less brittle leather from animal skin. Schiff† succeeded in producing such bodies from common phenol, pyrogallol, and phloroglucol. This appears to show that the properties of tannin are not dependent on the CO group, but rather on the general structure.

Gallotannic acid is met with, in commerce, in the form of light buff-coloured scales, with a faint peculiar odour and a powerfully astringent taste. It is soluble in six parts of cold water or glycerin, and very readily in hot. It is also very soluble in alcohol containing water, but much less so in absolute. It is moderately soluble in washed ether, but scarcely at all in anhydrous ether, chloroform, benzene, or petroleum spirit.

The commercial acid usually contains more or less of gallic acid, which may be detected by dissolving in water, shaking with ether, and after decanting and evaporating the ether, applying the tests described under gallic acid (p. 120). It may also be frequently distinguished in the simple aqueous solution of the tannic acid by the same tests. Hot solutions of tannin will dissolve large quantities of gallic acid, which remains for long periods in a state of supersaturation, and if the solution be precipitated with salt, most of the gallic acid is thrown down with the tannin.† Commercial tannic acid in addition to its natural impurities, such as gallic and ellagic acids and glucose, is occasionally adulterated with starch.

* Annalen, clxxviii. p. 171.

† Schiff, *Gaz. Ch. Ital.* ix. pp. 1-22.

Gallotannic or digallic acid has never been crystallised, and so-called "crystal tannin" is merely a commercial product made by drawing the syrupy solution into threads which are broken up after drying, and resemble needle-crystals.

Gallotannic acid, like all other pyrogallol tannins, when treated with bromine-water, yields soluble bromine derivatives.

Gallotannic acid may be estimated by the various methods given in Sections XIII. and XIV. for the estimation of tannin, but no rigidly accurate method of separating it from gallic acid and other impurities is yet known.

Some additional reactions of gallotannic acid will be found in Table V. p. 162. It is distinguished from gallic acid by its power of precipitating gelatin and many organic bases, including strychnine, quinine, cinchonidine, morphine, brucine, benzidine and all the "basic" coal-tar colours; and by giving precipitates with lead nitrate, lead acetate acidified with acetic acid, and ammoniacal solutions of copper and zinc sulphates.

Ellagitannic Acid is generally associated with gallotannic acid in tanning materials of the pyrogallol group, varying in proportion, from large quantities in divi-divi, myrobalans, and valonia to mere traces in sumach. Either it, or some analogous body producing bloom, is also present in considerable proportion in oak bark, associated with a catechol tannin. Ellagitannic acid is noteworthy as the source of bloom, or ellagic acid (p. 121) which see. Its constitution is quite unknown, and it may be merely a hydrated colloidal soluble form of ellagic acid, but is more probably a soluble glucoside of it, which is easily split up by ferments, or even by simple boiling; or even a compound of ellagic and gallic acids, as suggested by Perkin.

It is probable that other tannins of the pyrogallol group exist, especially as alkylated digallic derivatives with the properties of tannins can be formed synthetically (p. 134), but so far, none have been recognised or separated in nature. It is highly probable that the tannins of valonia, oakwood-extract, and myrobalans, and several other pyrogallol tans are not actually identical with digallic acid, though evidently closely related. The tannin of babool pods (*Acacia Arabica*, and some other allied species), though belonging to this group, is evidently not identical with digallic acid, as it gives no insoluble precipitate with lime-water.

The Catechol Tannins, like the pyrogallol tannins, form a class which contains more than one member, though it is likely that many tannins which have received different names are mixtures of comparatively few individuals.

• Schiff has shown that aqueous solution of protocatechuic acid, after boiling for some hours with arsenic acid and treatment with ether, separates into three layers, of which the middle yields diprotocatechuic acid, $C_{14}H_{10}O_7$, analogous to digallic acid, and resembling it in most of its properties, but giving green coloration with ferric chloride*. He also obtained a "tetraprotocatechutannic acid" by the action of phosphorus oxychloride on an ethereal solution of protocatechuic acid. It seems not improbable that such condensation products exist, containing two different acids, and hence, like some of the natural tannins, yielding more than one phenol on decomposition. Whether the natural catechol tannins are of so comparatively simple a constitution is yet doubtful, but the solution of the problem is much complicated by the difficulty of separating amorphous and closely allied bodies. All catechol tannins contain a protocatechuic acid group, but some yield phloroglucol and others do not. To the first of these classes belong the tannins of cutch and gambier (catechus), whence the name is derived.

Catechutannic Acid is obtained from gambier and cutch. It is not improbable that the two products are identical, but uncertain whether the apparent differences are due to impurities or variations in constitution, and it is very possible that both are mixtures of more than one chemical individual. Closely allied tannins are found in kino and many other plants. The tannin of gambier seems to possess important practical differences from other catechol tannins, being less astringent, and more readily removed from leather by washing.

Catechutannic acid appears to be an anhydride or mixture of anhydrides of catechins, though it is quite possible that catechu also contains tannins not derived from catechins.

Catechins.—It was formerly supposed that the catechins from different sources were identical. Recent researches, however, especially those by Perkin and Yoshitake† show that the catechins are a class containing at least two or three distinct

* Ber., 1882, xv, p. 2588.

† Journ. Chem. Soc., lxxxi. 1892, p. 1160.

chemical individuals closely resembling each other in properties, and probably also in constitution.

Gautier* appears to have been the first to show that there was more than one catechin, and indeed describes three isolated from gambier (from *Nauclea Gambir*): (a) with melting point 204° – 205° C.; (b) m.p. 176° – 177° C.; (c) m.p. 163° C. He further describes several other catechins of different melting points derived from acacia catechus. Perkin and Yoshitake (*loc. cit.*) working on cube gambier, which was extracted with ethyl acetate and the product purified by crystallisation from water after fractional precipitation with lead, obtained a catechin agreeing in melting point with Gautier's (b), which appeared to be a chemical individual, but could not detect the (a) catechin. Dried at 100° C. the air-dried crystallised substance lost about 20 per cent. of water of crystallisation, and on subsequently heating to 160° C. no further loss or change beyond slight browning occurred. Analysis gave numbers closely approximating for the crystalline substance to those required for $C_{16}H_{14}O_6 \cdot 4H_2O$, and this formula was further confirmed by analyses of azobenzene benzoyl and acetyl derivatives. Molecular weight determinations by the freezing point method in naphthalene gave results confirmatory of the formula just quoted, and acetylation and benzooylation indicate five replaceable OH groups. By treatment with lead acetate in solution slightly acidified with acetic acid, a crystalline lead salt, corresponding to the formula $C_{16}H_{14}O_6 \cdot Pb(C_2H_3O_2)_2$ was obtained. The catechin was sparingly soluble in cold water, freely in alcohol, and if air-dried, soluble in ether and ethyl acetate, but not if dried at 100° C. It gave the phloroglucol reaction with deal-shaving and hydrochloric acid, and on fusion with potash, phloroglucol and protocatechuic acid, and a volatile acid, probably acetic. With ferric chloride a green, and in presence of sodium acetate a deep violet coloration was produced.

From the mother liquors formed in purifying this (b) catechin a second catechin was isolated, with a melting point of 235° – 237° C., and crystallising without water of crystallisation. In its other properties, and decomposition-products, as well as in the results of ultimate analysis, it was identical with catechin (b).

From acacia catechu ("kath") the same authors obtained a

catechin, which sinters at about 140°C ., resolidifies, and finally melts at $204^{\circ}\text{--}205^{\circ}\text{C}$. without decomposition, and which was possibly identical with Gautier's (a) catechin. Except in melting point, it appears to be identical in properties and composition with catechin (b).^{*} The authors state that all these catechins are probably represented by the formula $\text{C}_{15}\text{H}_{14}\text{O}_6$, but are different substances, since they differ not only in melting point but in water of crystallisation, and similar differences occur in their derivatives. It is possible that the volatile acid obtained on potash-fusion is in some cases formic and not acetic. The work of Perkin and Yoshitake has on many points been confirmed by that of Kostanecki and Tambor,^{*} and Karnowski and Tambor.[†] Ordinary gambier catechin yields a series of reds, probably anhydrides, on boiling with dilute sulphuric acid. Heated in dilute sulphuric acid 1:8 in a sealed tube to 140°C . catechol and phloroglucol together with a red anhydride are obtained. In concentrated sulphuric acid, it dissolves with a deep purple coloration. It is readily soluble in alcohol and in boiling water, but requires about 1100 parts of cold water for its solution. Hence it separates on cooling from a hot solution of gambier, and may be purified by redissolving in hot water and treatment with animal charcoal, and subsequent crystallisation. The white deposit on pit sides and on the surface and interior of leather, which is often found when gambier is largely used, and which is sometimes called the "whites," consists of crystallised catechin. It may be dissolved by warm water or liquors, or may be decomposed by warm sulphuric acid. This deposit is favoured by the use of *hot* gambier liquors, from which it crystallises on cooling. Its occurrence has also been attributed to some kind of fermentation of gambier liquors, but this is very doubtful. Catechin may be extracted from its aqueous solution by agitation with ether. It possesses no acid properties, though some writers have incorrectly called it catechuic acid. The aqueous solution gives precipitates with albumin, lead acetate, and mercuric chloride, and reduces ammonio-nitrate of silver; but, unlike tannins, it does not precipitate gelatin, alkaloids, or tartar emetic. It is oxidised by permanganate in presence of free acid, and hence, when in solution, is estimated by the Löwenthal method as "non-tannin." It is also partially absorbed by the hide powder filter

so that the analysis of gambiers by this method is rendered difficult and uncertain. It probably possesses no tanning properties itself, but its anhydrides will tan. In experiments made by the writer a slight tanning effect was observed in a cold saturated solution, which had a faint yellow colour and probably contained a trace of anhydrides, and on boiling the solution for some time, the tanning effect was increased and both the liquid and the leather took a deeper and redder colour. Its value is therefore uncertain, but the practical results from gambier seem larger than corresponds to the ready formed tannins present, and it is not improbable that in the tanning process the catechin is gradually converted into available tannins. Hunt has, however, shown* that, as estimated by the Löwenthal process, the tannin in gambier is to some extent lessened by boiling, probably by conversion into an insoluble anhydride. Although the tannins of gambier and cutch are so nearly related, great differences exist in their tanning properties.

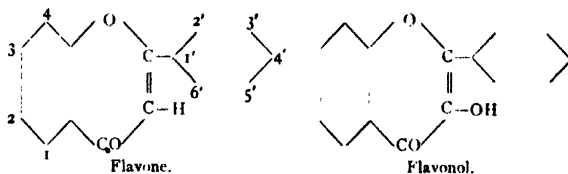
Natural Colouring Matters allied to Tannins.—These are so constantly present in vegetable tanning materials, and so frequently influence their colour reactions, that a section on the Chemistry of Tannins can hardly omit some notice of them; and as they are closely allied to tannins in their products of decomposition, and are moreover crystalline bodies, the structure of which has been closely investigated by many chemists, and especially in recent years by A. G. Perkin and by Kostanecki and their pupils, and which is now comparatively clearly understood, their study can hardly fail to cast light on that of the tannins themselves.† Their relation to tannins has already been mentioned on p. 104. Like the tannins, they usually occur in nature as glucosides, generally crystalline, which are broken up by digestion with dilute acids, or by ferments, leaving the colouring matters themselves as crystalline powders, usually very sparingly soluble in water, but pretty freely so in alcohol, especially with the aid of heat. They are usually precipitated by lead acetate, which, however can frequently be used in their purifica-

* Journ. Soc. Chem. Ind., 1885, p. 266.

† The best summary of present knowledge of the natural colouring matter is "*Die Chemie der natürlichen Farbstoffe*," by Dr. H. Rupp (Vieweg und Sohn, Braunschweig). Their occurrence in tanning materials has been specially studied by Perkin in a series of papers communicated to the Chemical Society; Chem. Soc. Trans., 1890, lix. pp. 1289, 1299, 1303; 1897, lxxi. pp. 1131, 1194; 1898, lxxiii. pp. 374, 1016.

tion, tannins and phlobaphene bodies usually coming down in the first fractions. The colouring matters found with tannins mostly dye more or less pronounced yellow shades on tin and alumina mordants and olives on chrome and iron, and belong to one group, the *flavones*. Others such as hæmatoxylin and brasilin from logwood and Brazil-wood are more or less associated with tannins, but hardly come within the scope of this section.

Flavone, the at first hypothetical type of the group actually synthesised by Kostanecki, * and its derivative *flavonol* possess the constitutions shown below; and the colouring matters in which we



are specially interested, quercetin, fisetin, myricetin, and morin are all derived from the latter, and differ only in the number and arrangement of OH groups on the two benzene rings. All but fisetin, the colouring matter of *Rhus cotinus* ("Venetian sumach" or "young fustic"), have OH groups in the 1, 3 positions. When these are fused with potash, the intermediate (pyrone) ring is broken and OH substituted for the OC in the 5' position, so that phloroglucol is formed, though it does not actually exist in the colouring matter, which therefore does not give the pine-shaving reaction. Fisetin has no OH in the 1 but only in the 3 position, and therefore yields resorcinol on fusion. Quercetin and fisetin have OH groups in the 3' and 4' positions on the second ring, which on fusion becomes oxidised to protocathechuic acid, while morin, the colouring matter of *Morus tinctoria* (fustic), has OH groups in the 2' and 4' positions, and yields resorcinol but no protocathechuic acid in addition to phloroglucol. Myricetin, the colouring matter of many sumachs and of *Myrica nagi*, has OH groups in the 1, 3, and 3', 4', 5' positions, and consequently yields phloroglucol and gallic acid on potash-fusion. Several of these flavones yield, in addition to the products named, acetic, glycolic or oxalic acids from the residues of the pyrone ring.

* Ber., xxvi. p. 2901; xxviii. p. 2302

It is interesting to compare the behaviour of these flavones with maclurin, or so-called "moringatannic acid," a second crystalline colouring matter of fustic, which not only yields phloroglucol on potash-fusion, but gives the pine-shaving reaction.

The structure of maclurin is probably $\text{OH} \begin{array}{c} \text{OH} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_2 \\ \diagdown \quad \diagup \\ \text{OH} \end{array} \text{CO} \begin{array}{c} \text{OH} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_2 \\ \diagdown \quad \diagup \\ \text{OH} \end{array} \text{OH}$,

so that the phloroglucol exists ready formed in the substance. In this respect it resembles the catechins.

Quercetin, with its glucosides, is the commonest colouring matter in tanning materials, and is the principal one of quercitron (*Quercus tinctoria*), and is also found in quebracho, cape sumach (*Osyris compressa*), gambier, the acacias, and many other materials, while myricetin is common in the sumachs, and some other tans of the pyrogallol class.

Other Natural Tannins.—It can hardly be said that any natural tannins except digallic acid have been thoroughly investigated, and most of them have not even been prepared in a state of approximate purity. It is known that tannins of the pyrogallol class exist in many plants, but whether these are merely impure forms of digallic acid and its glucosides or allied tannins of different constitution containing perhaps methyl or other alkyl derivatives of pyrogallol, is by no means decided in most individual cases. There is probably little doubt that the principal if not the only tannin of sumach and most galls is gallotannic acid, and apart from the soluble tannin of ellagic acid, the same is probably true of myrobalans, but is by no means so certain with regard to divi-divi, or chestnut-wood and oak-wood tannins, and many others. Böttinger* believes oak-wood tannin to be a methyl derivative of digallic acid, of the formula $\text{C}_{18}\text{H}_{12}\text{O}_9 \cdot 2\text{OH}_2$, which loses one molecule of water at 100°C . and the second at 135°C . He obtained a pentacetyl derivative $\text{C}_{18}\text{H}_7\text{Ac}_5\text{O}_9$, and two bromine derivatives from this, $\text{C}_{18}\text{H}_{10}\text{BrAcO}_9$ and $\text{C}_{18}\text{H}_7\text{Br}_4\text{AcO}_9$. Koerner† acetylated oak-wood and chestnut-wood tannins, and found for the former an acetyl derivative containing 5 acetyl groups (31.8 per cent.) and with a molecular weight (by freezing-point in phenol) of 689 approximately. Böttinger's formula gives a molecular weight of 546 and 39.4 per cent. of acetyl ($\text{C}_2\text{H}_5\text{O}$), while if Koerner's results can be accepted as reliable,

* Ber., xx. 1887, pp. 761-766.

† Koerner, Collegium, 1903, p. 163.

the constitution must be much more complex. He, however, points out himself that with such substances cryoscopic methods are not very reliable. Koerner (*loc. cit.*) found for the acetyl compound of chestnut-wood tannin a molecular weight of 870 and 36.5 per cent. of acetyl, so that he considers it to contain 7 acetyl groups, and states that the acetyl compound differs in solubility and other properties from the oak-wood derivative, and that therefore the two tannins are distinct. Considering the many sources of error to which such determinations are liable, these results must be accepted with a certain reserve. It is possible that many apparent discrepancies arise from the difficulty of distinguishing between the tannins and their glucosides.

With regard to the tannin of algarobilla pods (closely allied botanically to divi-divi) Zolfel* states that they yield 8-10 per cent. of gallotannic, and a much larger quantity of ellagitannic acid. The gallotannic acid exists as a glucoside with dextrose. The ellagitanic acid (p. 136) is free from glucose, and takes 5 acetyl groups. He believes it to be isomeric with digallic acid $C_{14}H_{10}O_9$. As ellagic acid is now known to be $C_{14}H_6O_8$, and to separate almost spontaneously from the ellagitannic acid, it is difficult to see how this constitution is possible. Zolfel believes the tannins of algarobilla to be identical with those of myrobalans.

Some pine-tannins apparently contain pyrogallol derivatives. The bark of the silver fir (*Abies pectinata*) is said to give a blue-black with ferric salts. G. Heyl† has investigated the tannin of the cones of *Sequoia gigantea*, the giant pine of California, which gives a brownish-black with ferric chloride, and insoluble precipitates with salts of Ba, Mg, Cu, and Pb, which, when heated to 200° C. yield pyrogallol. Boiled with dilute sulphuric acid, insoluble reds, and only small quantities of glucose and of gallic acid are produced. Heyl gives the constitution of the tannin as $C_{21}H_{20}O_{10}$, and of its bromine and acetyl derivatives as $C_{21}H_{18}O_{10}Br_2$ and $C_{21}H_{14}O_{10}(C_2H_5O)_4$ respectively, but these formulæ, like most others which have been given for tannins must be accepted with much reserve.*

Turning to catechol tannins, it is pretty certain that wider divergences exist. None of the natural tannins can be simply diprotocatechuic acid $C_{14}H_{10}O_7$ (p. 137), since it contains only

* Arch. Phar., cccxix. pp. 123-150; J. am. Chem. Soc. Abst., 1891, p. 918.

† Chem. Centralb., 1901, ii. p. 312.

57.93 per cent. of carbon, while Trimble points out that the natural catechol tannins contain about 60 per cent. (p. 108). It does not appear that they are usually glucosides, the principal products on boiling with dilute acids being insoluble reds, which are probably condensation products, possibly anhydrides, of the tannins.

Quercitannic Acid. Oak-bark tannin.—This tannin may be prepared from oak bark by Prof. Trimble's method, described on p. 111, who obtained the oak tannins as light-coloured powders very similar in appearance to gallotannic acid, and easily soluble in water and other solvents of gallotannic acid.

It may also be prepared by evaporating the alcoholic extract, and extracting with water, which leaves the phlobaphenes or higher anhydrides undissolved. The first anhydride, which is partially soluble, may be precipitated by the addition of salt, and the quercitannic acid extracted by shaking the filtered solution with acetic ether. In very dilute alcohol it yields a pure yellow precipitate with lead acetate. In aqueous solution the precipitate is light brown. When pure, quercitannic acid gives a green-black with ferric salts, and yields nothing to pure ether or to benzene. The blue-blacks given by many oak-bark infusions have been shown by Trimble to be due to the presence of colouring matters, which in some cases can be isolated by removing the tannin with neutral lead acetate, and after filtration precipitating the colouring matter with the basic salt.

If quercitannic acid be heated to 130°–140° C., it loses water and yields a red anhydride slightly soluble in water, which constitutes the red colouring matter of oak bark and which has also been called "difficultly soluble tannin." It precipitates gelatin, and is one of the class which Eitner well designates "tanning colouring matters." It gives a brownish red with lead acetate and a blue-black with ferric salts; it is difficultly soluble in water and ether, but readily so in alcohol of all strengths. Together with other anhydrides, it exists naturally formed in the bark. At higher temperatures, or by boiling with acids, a series of higher anhydrides may be obtained which are quite insoluble in water, but are soluble in alcohol and caustic alkalies. No glucose is produced by treatment of pure quercitannic acid with acids, that found after so treating oak-bark extract being due to the levulose present. If oak-reds are fused

with potash they yield, according to Johansen,* protocatechuic and butyric acids, while both Etti and Böttinger obtained protocatechuic acid and more or less phloroglucol. It must not be forgotten that many if not all oak-barks contain quercetin, and that this if not completely removed must yield protocatechuic acid and phloroglucol on potash-fusion, but many oak-barks give a faint reaction with pine-shaving and hydrochloric acid, while quercetin does not do so. If heated in sealed tubes with fuming hydrochloric acid, methyl chloride is evolved and red anhydrides and traces of gallic acid formed. The constitutional formula of quercitannic acid is as yet very uncertain. It is known that the tannin of oak wood differs materially from that of the bark, the former being a pyrogallol and the latter a catechol derivative, and it is doubtful whether either has been isolated in a state of purity, or free from traces of colouring matters. Trimble's tannins from different oaks, which were probably among the purest yet prepared, showed slight differences in properties which may have been due to difference of constitution, but more probably to residual impurities. Trimble detected catechol in the product of oak-bark tannins heated in glycerin, and protocatechuic acid in those of the action of hydrochloric acid and of fused potash. Pyrogallol, gallic acid and phloroglucol were not detected. The average of nineteen ultimate analyses of tannins of different species of oak is given by Trimble as $C = 59.79$, $H = 5.08$, $G = 35.13$ per cent. This agrees fairly well with Etti's formula for the tannin of *Quercus pubescens*, $C_{24}H_{20}O_6$, but he states that his tannin was insoluble in water (and hence perhaps an anhydride). Elaborate researches have been made on the constitution of oak tannins by Löwe, Etti and Böttinger, with somewhat contradictory results. For details the original papers must be consulted, references to which are given below.† A

* Arch. Pharm., [3] ix. p. 210; Chem. Soc. Journ., 1877, i. p. 721.

† Papers referred to on the constitution of quercitannic acid:—

1880. C. Etti, 'Monatshefte für Chemie,' i. p. 262; Ch. Soc. Abs., 1881, p. 277; C. Böttinger, 'Annalen der Chemie,' ccii. p. 263.
 1881. C. Etti, Berichte d. Deutsch. Ch. Ges., xiv. pp. 1398, 1826 (Ch. S. Abs., 1881, p. 1021); ibid. p. 2390; Dingler, ccxli. p. 69; J. Löwe, Zeits. Anal. Ch., xx. p. 208.
 1883. Böttinger, Berichte, xvi. p. 2710, and Ch. Soc. Abs., 1884, p. 321; Etti, Monatshefte, iv. p. 512 (Ch. Soc. Abs., 1883, p. 994).
 1884. Etti, Ber., xvii. p. 1820 (Ch. Soc. Abs., 1884, p. 1355); Böttinger, Ber., xvii. pp. 1041, 1123; Ch. Soc. Abs., 1884, p. 1025.
 1887. Böttinger, Annalen, ccxxxvii. p. 336; ibid. ccxl. p. 330; Ber., xx. p. 761.
 1888. Etti, Monatshefte, x. pp. 647 and 805.

good summary is given by Trimble.⁴ For the reactions of various oak tannins and infusion see p. 163.

On the whole, it seems probable that the principal tannin of oak bark is a purely catechol tannin, and that the gallic and ellagic acids, which have been detected in it, are due to an admixture of the gallotannic and ellagitannic acids present in oak wood, galls, and probably more or less throughout the tree. Apparently phloroglucol is present, but in very much smaller quantity than in gambier. It is not improbable that the tannins of hemlock and mimosa are identical with the catechol tannin of oak bark.[†] Böttinger, however (*loc. cit.*), gives the following percentages of bromine as contained in the precipitates from aqueous solutions of their tannins, which do not support their identity.

Oak bark, brownish	yellow precipitate	28.4	per cent. Br.
Hemlock bark and	} reddish yellow precipitate.	42.1-43.5	,, ,,
Quebracho wood			
Mimosa and chest-	} pale yellow precipitate	49.3-53.2	,, ,,
nut barks, gambier			

SECTION IX.

THE QUALITATIVE RECOGNITION OF TANNING MATERIALS.‡

THIS has become a matter of considerable importance, since the commercial value of an extract is dependent, not only on the percentage of tanning matter as determined by analysis, but on the nature of the tannin present which influences the character of the leather produced. It is also frequently desirable to ascertain what material has been used in tanning a given leather, and though in mixed tannages it is impossible to determine this accurately, chemical tests applied to the extract of the leather will frequently give much useful information.

It is obvious that, failing a clear knowledge of the tannins themselves, any really scientific scheme of separation is for the present impossible; since, although we know that the tannins are

* 'The Tannins,' i. p. 94.

† See Böttinger, *Ber.*, 1884, xvii. p. 1123.

‡ *Cp. Journ. Soc. Chem. Ind.*, 1894, p. 487; 'Gerber,' 1894, p. 195.

a class, we are quite ignorant of their number, which may be a comparatively small one, because many members of the group which at present receive individual names are probably mere mixtures. All that can be so far done is to separate the tanning materials into groups or individuals by reactions which have been empirically determined; of which in many cases we do not know the chemical significance, and which are often due to other constituents of the materials than the tannins themselves. The question is still further complicated by the fact that wood, bark and fruit of the same tree often yield tannins of distinctly different character. Thus the bark of *Acacia arabica* (Babul) gives the general reactions of the Australian acacias, and evidently contains as its main constituent a tannin of the catechol group; while the pods of the same tree have a tannin which differs from any other which I have examined, but which is apparently a pyrogallol derivative. The differences between the tannins of oak bark, galls and wood are equally striking. And while cutch from the wood of *Acacia catechu* gives the phloroglucol reaction intensely, the bark of the same tree hardly contains a trace.

In the previous Section it has been shown that the foundations of a clearer knowledge are being laid, and while we must still take advantage of any reactions which enable us to recognise individual materials, there are certain broad distinctions of a chemical nature which we can already utilise as the basis of a classification, which we may hope to subdivide further as our knowledge increases. It must, however, be borne in mind that, for commercial purposes, the problem is not always the recognition of chemical individuals merely, but of their origin. It is very probable, for instance, that the principal tannins of oakwood and divi-divi are identical; but their commercial value in an extract may differ considerably from the presence or absence of other constituents characteristic of the several materials. Some of these constituents may be removed or altered by the processes of decolorising and rendering soluble now used in extract manufacture, so that it often happens that reactions quite characteristic of the original material may be absent in its purified extract.

We may make the beginning of a scientific classification by dividing "catechol tannins," derivatives of the dihydric phenol catechol, and of its corresponding protocatechuic acid, from

"pyrogallol tannins" derived from the trihydric phenol, pyrogallol, and its corresponding gallic acid. To do this no elaborate separation is necessary, for not only do the two classes differ markedly in general character, but they are distinguished by the fact, not yet explained, but apparently without exception, that while dilute solutions of catechol tannins give an immediate precipitate with bromine water, and form insoluble bromine-derivatives, the corresponding derivatives of pyrogallol tannins are soluble and do not precipitate except in a few cases after long standing and probable oxidation. Again, when all pyrogallol tannins give blue-blacks with neutral ferric salts, most catechol tannins (and perhaps all if properly purified) give green-blacks. The principal exceptions to this rule are the Australian mimosas which give violet-blacks, and oak-bark of *Quercus robur* which gives a blue-black, probably from the presence of pyrogallol derivatives, since its purified tannin gives the usual green-black. A crimson reaction with concentrated sulphuric acid is also usually a distinguishing mark of the catechol tannins.

Another instance in which definite knowledge of constitution may be obtained by a qualitative test is that of the catechol tannins which also contain phloroglucol, and which consequently give a pink or violet coloration to deal-shaving when moistened with hydrochloric acid. The most pronounced instances of this are the true catechus from *Nauclea gambir* and *Acacia catechu*, though many other materials give a faint reaction. It is pointed out on p. 145 that many bodies such as quercetin, which yield phloroglucol on fusion with potash, do not contain it ready formed, and consequently do not react with deal-shaving, and the same is probably the case with some of the tannins. It must also be remembered that resorcinol, and probably some of its derivatives, give a bright blue coloration under the same test.

The other reactions used in the following tables are more of the nature of special tests, and in most cases the chemical changes involved are not understood. With many materials characteristic colour-changes take place from gradual oxidation when a tanning solution is treated as in the Payne and Parker method of analysis with large excess of a sugar-lime solution, or of baryta water.

In some cases valuable information as to constituents and even as to proportions of mixture may be obtained from quantitative methods. The relation between the quantities of tanning and soluble non-tanning substances present is often characteristic ;

and inferences may be drawn from the relation between the results of the gravimetric (hide-powder) method of estimation and those of Löwenthal's or Payne and Parker's, since in both of these a different factor is required for catechol and pyrogallol tannins.

For purposes of recognition, infusions of tanning materials may therefore be divided into three classes, as in Table I., viz. (1) Those which give a precipitate with bromine water, and green-black with iron alum, and which are pretty certainly catechol tannins; (2) those which give a precipitate with bromine water, but bluish- or violet-blacks with iron, and which for the present must be regarded as mixed or uncertain; and (3) those which give no precipitate with bromine, and blue-black with iron, and which, so far as we know, are all derivatives of pyrogallol.

These classes may be further subdivided by other reactions, but until the causes of these reactions are better understood, the classification must be regarded as somewhat artificial, since though convenient as an index, it sometimes happens that tannins probably really closely allied fall into different groups.

The strength of the infusions employed is understood to approximate to that used in the I.A.L.T.C. method for purposes of quantitative analysis, that is, containing about 0.4 per cent. of tanning matter; and the table on p. 191 will give a general idea of the weight of material which should be used.

The method of carrying out the various reactions is as follows:—

Bromine Water Reaction.—It is best to add the bromine water drop by drop to 2–3 c.c. of the infusion in a test-tube, until the solution smells strongly. In some cases the precipitate is slight, or forms slowly, and occasionally it is crystalline, and on this account less conspicuous, but it is usually a distinct yellow or brown flocculent one. In general terms bromine may be said to be a reagent for the catechol tannins; precipitating all which give green-blacks with iron, and many which give blue- or violet-blacks, which are reasonably suspected of containing catechol. It does not precipitate any recognised pyrogallol tannin, but several which yield ellagic acid (bloom), such as oak barks. No notice need be taken of any precipitate, which only forms after long standing, as bromine acts as an oxidising agent as well as directly, and many pyrogallol derivatives yield insoluble oxidation-products. For this reason it is desirable that

the bromine water should not be too strong; 4-5 grm. bromine per liter being suitable, and the solution of the tannin should be faintly acid, acetic acid being added if required.

Ferric Alum, Ammonium Ferric Sulphate.—A 1 per cent. solution of this salt has been chosen as easily obtainable, neutral and in a state of approximate purity. This salt forms violet crystals yielding a pale yellow-brown solution, which should not be kept too long, as it deposits iron as a basic salt. Ferric chloride, which is generally used, is almost invariably strongly acid, and of a very persistent yellow; and in excess will give a green-black reaction with gallotannic acid itself, and its results as a test are often misleading. Ferric acetate, which has also been recommended, gives heavy precipitates with most materials, and is very strongly coloured, so that it is found less convenient than the iron alum. As the colorations are generally very powerful, they are best seen by diluting the tanning infusion freely, and adding the iron solution very cautiously. In many cases the coloration first produced, and which is the characteristic one, rapidly fades to a dull olive or brown in presence of excess of iron, probably by oxidation and destruction of the tannin.

By far the largest number of tannins fall into Class I., giving precipitates with bromine and green-blacks with iron, but these may be pretty satisfactorily subdivided by a reaction with—

Cupric Sulphate and Ammonia.—When solution of cupric sulphate is added to a tanning material infusion, it sometimes gives a precipitate, and sometimes not. This distinction is of little importance, as the presence of any salt of a weak organic acid would in all cases cause a precipitate, by neutralising the sulphuric acid of the sulphate. Cupric acetate produces a precipitate with all tannins, so far as I have observed, and it is interesting to note that in this case, as in many others of a like character, the tannin combines with, and precipitates the salt as a whole. On the addition of ammonium carbonate, effervescence takes place, and the precipitate darkens, and becomes a true tannate.

When ammonia is added to the mixture of a tannin and cupric sulphate, a precipitate is invariably formed in the first instance, consisting of a tannate of copper with variable quantities of blue cupric hydroxide. With excess of ammonia, the whole of this precipitate is in many cases dissolved, while in others an insoluble tannate remains. The latter is the case with all tannins

derived from gallotannic acid, and with many containing proto-catechuic acid, and forms a useful means of classification, though as yet the difference of structure to which it corresponds is unknown. The fact that hemlock and other pine barks, as well as cutch and gambier, yield cupric tannates soluble in ammonia, is an instructive commentary on processes which have been proposed for quantitative estimation by precipitation by ammonio-cupric solutions.

Where the precipitate redissolves, it generally does so with the production of either a greenish brown, or a purplish brown coloration, which in presence of a small amount of the blue ammonio-cupric sulphate, appears either as a green or a reddish violet. It need hardly be pointed out that to see this coloration well, the copper should be in the least possible excess. Hence it is desirable to use a very weak copper solution, say at most 1 per cent.

We thus obtain two sub-classes; α (Table II.), in which copper produces a precipitate soluble in ammonia, and β (Table III.), in which an insoluble precipitate is formed. It must be admitted, however, that while in many cases the distinction is well marked, there are cases in which the solubility or the reverse is only relative, and others in which the precipitate appears to be soluble or insoluble according to the amount of phlobaphenes and impurities present. The excess of ammonia used is also not without influence in some cases.

No attempt has been made to arrange systematically the results of the further reactions which are suggested to determine individual members, since in the main they correspond to no broad chemical demarcation, and in others they shade off by imperceptible degrees, so that it is only by taking all characteristics into account that any safe conclusion can be drawn. This is specially the case with the vanillin reaction for phloroglucol, which is given strongly by cutch and gambier, markedly by several other materials, and so faintly by many others that no sharp line can be drawn. The following reactions are those which I have employed for further distinction:—

Nitrous Acid Reaction.—This reaction is obtained by adding to a few c.c. of the very dilute infusion in a porcelain basin a distinct excess of freshly prepared solution or crystals of sodium or potassium nitrite, and then 3–5 drops of decinormal sulphuric or hydrochloric acid. In typical cases the solution instantly

turns pink or crimson, and slowly changes through purple to a deep indigo-blue, but in others, as sumach, where the reaction is feeble, and masked by other changes, the final colour is green or even brownish. In a large number of cases, nitrous acid produces a yellow or brown coloration or precipitate, but "reaction" in the tables invariably means a series of colour-changes as above described. Nothing can as yet be said on the nature of the chemical changes produced. The reaction is apparently given by all tanning materials which yield ellagic acid or "bloom," but not by ellagic acid itself, either natural or synthetic, nor by pure gallotannic acid. It is, therefore, probably a reaction of ellagitannic acid, and is valuable for subdividing the mixed and pyrogallol tannins. It may also be obtained faintly from some of the oaks, which give green-blacks with iron, and are therefore classed as catechol tans.

Stannous Chloride and Hydrochloric Acid.—This reagent consists in a strong solution of stannous chloride in concentrated hydrochloric acid. If about 10 c.c. of this are added to 1 c.c. of the tannin material infusion, in a porcelain basin, and allowed to stand for 10 minutes, coniferous tans, mimosas and some others give a very marked pink coloration. This is specially distinct in the case of larch bark. If a small piece of larch-tanned leather be steeped in the reagent, the coloration appears very strongly.

Deal-Shaving and Hydrochloric Acid, Phloroglucol Reaction. This reaction is due to the condensation of phloroglucol with the traces of the methyl-protocatechuic aldehyde (vanillin) always present in the wood of the *Coniferae* (cp. p. 116). A shaving or slip of any pine wood is moistened with the infusion, and then, either before or after drying, is again moistened with concentrated hydrochloric acid. In the case of cutch and gambier and a few other materials, and of solution of phloroglucol itself, the spot becomes at once a bright red or violet, but in many cases the reaction is faint, and only appears after some hours. A decided red reaction probably always indicates the presence of phloroglucol. The statement that catechol gives a similar reaction appears to be an error; but a violet-blue is given by resorcinol.

Sodium Sulphite.—A few drops of the tanning solution are placed in contact with a crystal of sulphite on a tile or in a basin. With valonia, a bright purplish pink is rapidly developed,

apparently by oxidation. Many other tanning materials produced red or pink colorations, but in no case so marked a reaction as valonia.

Concentrated Sulphuric Acid.—A test-tube is rinsed out with the infusion and drained, so that only about a drop remains, and about 1 c.c. of concentrated acid is cautiously poured into the sloping tube, so as to form a layer underneath the tanning solution. The ring of colour at the junction of the two liquids is noted, and then they are mixed by shaking and diluted with water. About half the materials give a deep purplish crimson, called simply "crimson" in the tables, and in many cases this is decidedly pink on dilution, while in others it is obscured by brown products formed by the heat of mixture. A large number of other materials give browns or yellows only, which, when intense, may appear red, but dilute to yellows or yellow-browns. Allen recommends the addition of the acid to the residue previously evaporated to dryness, to avoid the heating produced by the combination of the acid with water, but in the table the reaction with liquid is used. The crimson reaction is also given by the "non-tannin" residues of many catechol tannins, possibly from the presence of catechins. If the residue is rubbed up with a few c.c. of alcohol, a red colour after filtration denotes the presence of non-tanning matters yielding "reds," and a portion evaporated to dryness, or nearly so, will give a crimson coloration with sulphuric acid. This reaction was suggested by the late J. E. Hughes as a test for quebracho in oak-wood extract, and has proved very useful.* Of course, it might be caused also by the presence of other catechol tans.

Lime Water is a most useful reagent, being very varied in the colour of the precipitates it produces, and the changes they undergo by oxidation. The reaction is best seen in a shallow porcelain basin, and time must be allowed for the changes to take place. It may be safely added in considerable excess. Allen recommends the use of a nitrometer for this and similar experiments, as the reaction can first be studied in absence of oxygen, and then air admitted.

Similar colour-changes occur in Payne and Parker's lime-water process of tanning estimation, and are utilised by them as a means of distinction between different materials.

General Remarks.—The infusions are assumed to be of about the strength used in determinations by hide-powder, viz. about

0.6 grm. of dry soluble matter in 100 c.c.; but moderate divergences from this do not influence results. Of course, reactions which are feeble may be imperceptible with very dilute solutions, and, on the other hand, strong solutions will sometimes give precipitates where only colorations are noted with weak ones. As some of these reactions are dependent, more or less, on the concentration of the infusion employed, it is desired to experiment in the first instance with known materials in order to acquire a little experience of the exact conditions.

In some cases these tests are sufficient to detect the constituents of mixtures, but usually this will remain impossible till further and more distinctive reactions are discovered.

They can, of course, be applied to the recognition of tannages when excess is present in leather, which can be dissolved out with water; but the effect of dilute alkalies and other solvents on the reactions demands further experiment. For this purpose Andreasch's alcoholic reactions (pp. 164-167) are often more suitable.

There are one or two special reactions of tanning materials which cannot be conveniently included in the tables, and may therefore be named here. The bark of chestnut-oak (*Q. prinus*) contains a substance which possesses a strong blue fluorescence, especially in alkaline solution. It is well seen after precipitating the tannin and colouring matter with ammoniacal zinc solution. A somewhat similar body, æsculin, is contained in the bark of the horse-chestnut.

Dieterich* has shown that if an alcoholic solution of gambier from *Nauclea* (*Uncaria*) *gambir* be rendered strongly alkaline with sodium or potassium hydrate, and shaken with petroleum ether, the latter takes a powerful green fluorescence. The same result is obtained with an *unfiltered* aqueous solution to which alcohol is added, but not with a clear filtered solution, or with an unfiltered one without alcohol. It is, therefore, due neither to the tannin nor the catechin, but to some body soluble in alcohol, but insoluble in water. Dieterich believes that this is quite characteristic of *Nauclea gambir*, and this accords with the writer's experience, though Eitner states that he has obtained the reaction from a sample of *Acacia catechu*, which he believes to be genuine. According to Dieterich the fluorescence is due to

Pharm. Central-II.N.F., 1896, xvii. p. 855. Ber. Pharm. Ges., 1897, vii. p. 153.

a substance which can be shaken out of the petroleum ether with dilute sulphuric acid, and recovered by neutralisation and shaking out with ether, but which gradually decomposes, leaving a red phlobaphene-like body.

Andreasch, in his pamphlet on "*Sicilianischer Sumach und seine Verfälschung*," * gives special tests for *Pistacia lentiscus* and *Tamarix africana*, materials which are constantly employed as sumach-adulterants. He states that if a concentrated solution or small fragments of potassium cyanide be added to an infusion of tamarix alone or mixed with sumach, and not containing at most more than 0.75 per cent. of tannin, a dirty yellow flocculent precipitate is obtained on stirring, which settles rapidly; but no precipitate or only traces are obtained where pure sumach alone is used. The potassium cyanide must be pure and without excess of potassium carbonate. In the case of solutions containing *Pistacia lentiscus*, 40 per cent. formaldehyde solution added drop by drop in small quantity to the neutral infusion of the sumach produces a light ochre yellow precipitate which occurs even in the presence of great quantities of sumach, and renders possible the detection of small quantities of *pistacia* with certainty. The solution first becomes turbid, and then deposits a gelatinous precipitate, which is insoluble in cold water. The present writer has not succeeded in obtaining very decisive results with these reagents, but any considerable admixture of *pistacia* may be detected in pure sumach by the bromine-water test with which the catechol-tannin of *pistacia* yields a precipitate, while the pyrogallol-tannin of pure sumach does not, though on long standing it becomes turbid from oxidation-products. On the microscopic examination of sumach, see p. 407.

Ferdinand Jean† suggested the detection and even the titration of chestnut-wood extract in mixture with oak-wood by the fact that when iodic acid is added to an infusion of chestnut-wood extract, a certain quantity of iodine is liberated, which can be removed by shaking the mixture with a little bisulphide of carbon, and recognised by its violet colour, or titrated in the usual way with thiosulphate. Jean stated that this reaction was not given by oak-wood, quebracho, and a variety of other tannins; but Mr. Blockey and the writer observed distinct liberation of iodine, not only with oak-wood extracts of the best marks, but

* "Der Gerber," Vienna, 1898.

† Collegium, 1902, i. p. 283; and 1903, ii. pp. 25 and 45.

with infusions made direct from well verified specimens of oak-wood (both English and Slavonian) in the laboratory. It would be interesting, however, to inquire further into the causes of this reaction.

Formaldehyde reacts on phenolic bodies in the presence of a mineral acid such as HCl giving condensation products of the type $\text{HO} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$, and interesting results have been obtained by applying this reaction to the tannins. Jean and Frabot* have stated that this reaction causes a complete precipitation of all catechol tannins when the solution is distinctly acid, and that no pyrogallol tannin is precipitated under these circumstances, though there is a partial precipitation when the solution is neutral. They have proposed, therefore, to estimate the catechol tannins in tanning materials by weighing the precipitate produced, and to detect the adulteration of pyrogallol tanning matters with materials containing catechol tannins, e.g., sumach with pistacia. Stiasny† and Nierenstein,‡ however, have not been able to confirm the value of this reaction, as they have obtained precipitates with pyrogallol tannins alone.

A method of distinguishing tanning materials which is sometimes useful, though not generally sufficient for definite identification, is that of dyeing the mordanted striped cotton used for a similar purpose by dyers. Various patterns are in use, usually mordanted with iron and alumina, and mixtures of the two, the iron giving blacks of varying shade with the tannins, and the alumina showing the presence of mordant colouring matters such as quercetin (p. 142). In this connection it must be remembered that ellagic acid dyes a feeble yellow. The strips are conveniently boiled for 15 minutes with solutions of the tannins of a similar strength to those used for analysis. In some cases a further distinction may be obtained by boiling a portion of the dyed strip in a 0.1 per cent. solution of potassium bichromate.§ Mordanted strips have also been prepared with a much greater variety of metallic salts, and consequently a greater variety of colour reaction, but the writer has not been able to obtain these commercially.

* Collegium, 1906, p. 435; and 1907, p. 188.

† Gerber, 1905, p. 187.

‡ Collegium, 1907, p. 52.

§ In ordinary dyeing of unmordanted cotton with cutch, the material is boiled for an hour with about 10 grm. of cutch and 1-2 grm. per liter of copper sulphate, allowed to cool in the solution, and "saddened" by boiling with bichromate solution of $\frac{1}{4}$ -1 grm. per liter.

TABLE I.

PRELIMINARY CLASSIFICATION OF TANNING MATERIALS.

CLASS 1. (CATECHOL TANNINS.)

Br. Water produces a Precipitate.

Iron-Alum gives Greenish Blacks.

Copper Sulphate followed by Ammonia in Excess.

Precipitate redissolves.

1 α
TABLE II.

Precipitate does not redissolve.

1 β
TABLE III.

CLASS 2. (MIXED AND DOUBTFUL.)

Br. Water produces a Precipitate.

Iron-Alum gives Blue or Purplish Blacks.

TABLE IV.

CLASS 3. (PYROGALLOL TANNINS.)

Br. Water produces no Precipitate.

Iron-Alum gives Blue Blacks.

TABLE V.

TABLE II.

Catechol-tans giving greenish blacks with ferric alum, a precipitate with bromine water and crimson coloration diluting to pink with concentrated sulphuric acid, except where otherwise noted. *Copper precipitate soluble in ammonia.*

Class 1a.	Nitrous Acid.	CuSO ₄ + NH ₄ OH.	SnCl ₂ + HCl.	Deal Shaving and HCl.	Na ₂ SO ₃ .	Lime Water.	Remarks.
Cutch from <i>Ac. catechu</i> wood.	No react. darkens.	Pp. redissolves generally reddish coloration.	No react.	Deep violet-red.	Reddens somewhat.	Reddish pp. slowly formed.	Brownish red coloration with H ₂ SO ₄ . Contain quercetin.
"Thann leaf" extract (a cutch substitute) (<i>Terminalia Oliveri</i> .)	do.	Pp redissolves brownish coloration.	do.	No react.	No react.	No. pp.	Olive-black pp. with iron-alum.
"Tulwar bark" (<i>Casina auriculata</i>).	do.	Pp. redissolves reddish violet.	do.	Trace.	Pink coloration.	Reddish pp.	
Quebracho wood (<i>Loxopterygium Lorentii</i>).	do.	do.	do.	None or slight.	Slight pink coloration.	do.	Purified extracts react similarly. Extracts with oxidised tannins give insoluble pp. with copper.
"Tengah" bark (<i>Ceriops Candalliana</i>).	No react. darkens, pp.	do.	Pink.	do.	Pink coloration.	Bright red pp.	A mangrove much used in making extracts.
Bark (<i>Acacia leucophloea</i>)	No react.	do.	do.	Slow violet react.	do.	Dull brown pp.	
Bark (<i>Soyimida febrifuga</i>).	do.	Pp. redissolves reddish brown.	do.	No react.	do.	Red-brown.	
Cork Bark (<i>Quercus suber</i>).	Reacts somewhat.	Pp. redissolves brown.	No react.	do.	Reddens.	Reddish brown pp.	

Green oak (Ital.) (<i>Quercus ilex</i>).	Reacts faintly, if at all. Reacts?	do.	do.	do.	do.	do.	do.	Contains much quercetin, and dyes yellow on Al and Sn mordants.
Garonille (root bark of Kermes oak) (<i>Quercus coccifera</i>).	Reacts?	do.	do.	do.	do.	do.	do.	Alkaline solution yields fluorescent solution with petroleum ether, see p. 154. Contains quercetin.
Quercitron bark (<i>Quercus tinctoria</i>).	Reacts somewhat.	do.	Light green.	do.	Doubtful.	do.	do.	"Cape sumach" contains osyritin, a glucoside of quercetin, and a glucoside tannin.
Gambier (ext. of leaves of <i>Nauclia gambir</i>).	No react. darkens.	Pp. redissolves olive-green.	Yellow.	Deep violet-red.	Yellow.	No pp.	No pp.	A Natal sumach-substitute. H_2SO_4 gives dark brown.
"Pruin bast" (leaves of <i>Colpoon</i> or <i>Ostrya compressa</i>).	No react.	Pp. redissolves greenish.	No react.	Pink.	do.	Light yellow pp.	Light yellow pp.	H_2SO_4 gives brown-red, dilutes brown.
"Koko" (leaves of <i>Celastrus buxifolia</i>).	do.	do.	do.	No react.	do.	Bright yellow pp.	Bright yellow pp.	Olive-green coloration and reddish pp. with iron-alum.
Larch bark (<i>Larix euroj. za</i>).	No react. darkens.	Pp. redissolves olive-green.	Pink.	do.	No react. darkens.	Rusty pp.	Rusty pp.	<i>Rothanne</i> , <i>Fichte</i> , common spruce fir. Iron gives brownish green, and H_2SO_4 brownish red.
Hemlock bark (<i>Tsuga</i> or <i>Abies canadensis</i>).	No react., pink with $NaNO_2$. No react.	Pp. redissolves neutral fnt. Pp. redissolves olive-green.	do.	do.	Darkens.	Red-brown pp.	Brown pp.	Chile, tanning material of valdivia leather.
Lingue bark (<i>Persea lingue</i>).	Darkens	Pp. redissolves.	do.	Reddens slightly after standing. No react.	No react.	do.	do.	
Mallet bark (W. Austr.) (<i>Eucalyptus occidentalis</i>).	do.	do.	Slight or none.	No react.	Slight pink.	Brown pp. darkens.	Brown pp. darkens.	
Birch bark (inner) * (<i>Betula alba</i>).	do.	do.	No react.	Becomes slowly red, then violet.	Very slight pink.	Light brown.	Light brown.	

TABLE III.

Catechol-tans giving greenish blacks with ferric alum, a precipitate with bromine water, and crimson coloration with concentrated sulphuric acid, except where otherwise noted. · *Copper precipitate insoluble in ammonia.*

Class I β.	Nitrous Acid.	CuSO ₄ + NH ₄ OH.	SnCl ₂ + HCl.	Deal Shaving and HCl.	Na ₂ SO ₃ .	H ₂ SO ₄ .	Lime Water.	Remarks.
Willow bark (Russian. Sp. unknown). <i>Acacia anglica</i> or <i>Euphlatenia macrocarpa</i> bark <i>Acacia culcitra</i> bark	No react. do. do.	Dense pp. Dense chocolate pp. Dense violet-black pp.	No react. Pink or violet. Possible trace.	Violet faint. do. Trace.	Pink. Reddens somewhat. Pink.	Red-brown, not intense. Crimson dilutes pink. Red-brown.	Slight greyish pp. Reddish pp. Flesh colour pp.	
"Thorn tree" bark (<i>Acacia horrida</i>) Cape. Mangrove bark extract (<i>Rhinophora manglc</i>).	No react. darkens. No react.	Dense pp. Reddish-black pp.	No react. Slight reddening.	Doubtful. No react.	do. Slight reddening.	Dull crimson not intense. Red-brown.	No pp. Red pp. darkened by excess.	
Crude Quebracho wood extract (<i>Quebracho</i> or <i>Loxopterygium Lor-entzii</i>). "Sugar bush" bark (Cape) (<i>Protea mli-folia</i>).	do. No react. darkens.	Dense pp.* do.	Pink colour pp. No react.	Trace. do.	Doubtful. do.	Crimson dilutes pink. Red.	Light-brown pp. Yellow-brown pp.	Contains fisetin, and some ellagic acid. (* See also Table II.)
"Waagenboom" (Cape) (<i>Protea grandiflora</i>). "Kuppelboom" (Cape) (<i>Leucospermum cono-carpum</i>).	do. do.	do. do.	do. do.	do. Violet distinct.	Pink. do.	Crimson dilutes pink. do.	Light yellow pp. Slight greyish pp.	
"Silver tree" (Cape) (<i>Leucodendron argentea</i>). Chestnut Oak (<i>Quercus prinus</i>). Tamarisk (Brusa) (<i>Tamarix africana</i>).	do. Reacts distinctly. Doubtful.	do. Decided pp. pp.	do. do.	No react. do. Red on drying.	Pink. Reddens. Intense yellow.	do. do. do.	Flesh colour pp. Reddish-brown pp. Light yellow darkens.	Alkaline solution fluoresces blue. Gives <i>no</i> pp. with Br water. Contains ellagic acid and quercetin monomethyl ether.

Mixed and doubtful tans, giving blue- or violet-black with ferric alum, but precipitate with bromine water. Some react with nitrous acid and yield bloom.

Class 2.	Ferric Alum.	Nitrous Acid.	CuSO ₄ + NH ₄ OH.	SnCl ₂ + HCl.	Deal Shaving and HCl.	Na ₂ SO ₃ .	H ₂ SO ₄ .	Lime Water.	Remarks.
"Skens," Cyprus Sumach. (<i>Pistacia lentiscus</i>).	Blue-black pp.	No react.	Dark pp.	No react.	No react.	Yellow	Yellow-brown.	Yellow pp darkening.	"Schinia" "Leftisque."
Kliphaat bark (<i>Rhus Thunbergii</i>).	Blue-black	do.	Dense dark pp.	do.	do.	Pink.	Dull crimson dilutes orange.	Pinkish pp.	Cape Colony.
Canaligre (Root of <i>Rumex hymenosepalus</i>).	Blue-black pp.	do.	do.	No react. Clouds.	Trace violet.	Slight darkening.	Yellow-brown.	Pink coloration, greyish pp. Reddish-brown pp.	
"Talwaan" or "Elands-bontjes" (Root <i>Elephantorrhiza Burchellii</i>).	do.	No react. Darkens.	do.	No react.	do.	Pink.	Red.		South Africa.
Mimosa or Wattle barks (various Austral. <i>Acacia</i>).	Dirty violet pp.	No react.	Dense purple-brown pp.	Slight reddening.	Sometimes trace.	Reddens.	Crimson dilutes pink.	Reddish or yellow-brown pp.	
3abool bark, India (<i>Acacia arabica</i>).	do.	do.	Dense dark pp.	Some trace.	Faint trace.	Slight darkening.	Crimson dilutes orange.	Dark reddish-brown pp.	
Dark red Austr. bark (probably an <i>acacia</i>).	do.	do.	Deep violet pp.	No react.	do.	Orange pink.	Crimson dilutes pink.	Bright violet pp.	Needle crystals with Br.
"White bark" <i>Algaroba blanca</i> , South America (a <i>prosope</i> , or <i>acacia</i>).	do.	do.	Reddish-black pp.	do.	Violet.	Reddens strongly	do.	Red pp. turning violet.	
English Oak (<i>Quercus robur</i>).	Blue-black (green with excess).	Reacts somewhat.	Slight pp. Dark	No react.	Faint react.	Reddens.	Crimson dilutes pink.	Reddish-brown pp.	
Jaft or Dechift.† Stopped oak product.	Blue-black pp.	Reacts red-blue.	Brown pp. Dark	No react. Dark brown pp.	do.	Some darkening.	do.	do.	
<i>Africa nagi</i> .	Blue-black	Reacts.	do.	No react.	Very faint pink.	Slight pink.	Yellow-brown.	Brown pp.	

* Contains myricetin, some galloic acid, and a phloroglucol-catechol tannin (Parkin, Chem. Soc. Trans., 1898, lxxiii, p. 377).

† A Fersina product, dark scales very rich in tannin (about 40 per cent.). Strong infusions dry whitish and indurated.

TABLE V.

Pyrogallol-tans, giving blue-blacks with ferric alum and no precipitate with bromine water. Those which yield bloom (ellagic acid) give colour-change, red to blue, with nitrous acid. No pink coloration with $\text{SnCl}_2 + \text{HCl}$; no reaction with deal shaving (except babool pods).

Class 3.	Nitrous Acid.	$\text{CuSO}_4 + \text{NH}_4\text{OH}$.	$\text{SnCl}_2 + \text{HCl}$.	Na_2SO_3 .	H_2SO_4 .	Lime Water.	Remarks.
Allepoo galls (of <i>Quercus infectoria</i>).	Reacts red to blue.	Dark pp. insoluble.	Light yellow pp.	No react.	Greenish to dirty yellow.	Fale pp. turning bluish-green.	Contains myricetin
Sumach (leaf of <i>Rhus coriaria</i>).	Reacts feebly.	Dark brown insoluble pp.	No react.	do.	Yellow.	Yellow pp. turning bright green.	
"French Sumach" (<i>Cortaria myrsinolia</i>).	Reacts red to blue.	Pp. in solution.	Bright yellow.	Yellow.	Yellow-brown.	Olive-green pp.	Gives slight turbidity with Br.
Venetian Sumach (<i>Rhus cotinus</i>).	Reacts feebly.	do.	do.	do.	Yellow.	do.	Contains quercetin.
Myrobalans (<i>Terminalia chebula</i>).	Reacts red to blue.	Dark insoluble pp.	No react.	do.	do.	Yellow pp. turning greenish.	Much ellagic acid.
Pomegranate rind (<i>Punica granatum</i>).	do.	Dark brown insoluble pp.	do.	No react.	Orange-brown.	Bright yellow pp. turning red with excess.	Much ellagic acid.
Algarobilla (pod of <i>Cesalpinia brevifolia</i>).	do.	Dense dark pp.	do.	Deep yellow.	Deep yellow-brown.	Yellow pp. turning red-purple.	Contains much ellagic acid.
*Divi-Divi (pod of <i>Cesalpinia coriaria</i>).	do.	do.	do.	No react.	Crimson.	Yellow pp. turning black.	
Algarob (probably pod of <i>Prosopis dulcis</i>).	Reacts red to olive.	do.	do.	Yellow.	Yellow to olive.	Yellow pp. turning black.	
Valonia (cup of <i>Quercus Agilops</i>).	Reacts red to blue.	Dark reddish pp.	do.	Purplish pink.	Deep yellow.	Yellow pp. turning red-purple.	Contains much ellagic acid.
†Oakwood and chestnut-wood extracts.	do.	Purple-brown pp.	do.	Reddens.	Yellow-brown.	do.	
Pure gallotannic acid.	No react.	brown pp.	do.	No react.	do.	Pale pp. turning blue.	
Babool pods (<i>Acacia arabica</i>).	No react. darkens.	Dark pp. insoluble. green colour.	do.	do.	Reddish-violet.	Pink colour. No pp.	Faint violet with deal shaving and HCl.

* Moderate: strong potassium nitrite solution precipitates divi, but not *divi* oak-wood solutions; pp. soluble in hot, or much cold water.
† *Crode* chestnut wood extract may be obtained, had been obtained in the past.

TABLE VI.—REACTIONS OF PROFESSOR TRIMBLE'S PURIFIED OAK BARK TANNINS.*
 (* A monograph of the Tannins, vol. ii. p. 88.)

	Ferric Alum.	Bromine Water.	Nitrous Acid.	CuSO ₄ and Ammonia.	SnCl ₂ + HCl.	Deal Shaving and HCl.	Na ₂ SO ₃ .	Lime Water.
Black oak (<i>Q. tinctoria</i>) or Quercitron.	Green colour and pp.	Yellow pp.	Brownish-yellow pp. Pinkish colour, changing to brown pp.	Pp. Green colour.	Yellow with some pink.	Violet colour.	Yellow colour.	Pp. turning pink, then red.
Pin oak (<i>Q. palustris</i>).	do.	do.	Brown pp.	Pp. Brownish-green colour.	Pink colour.	do.	Pink colour.	do.
Scarlet oak (<i>Q. coccinea</i>).	Bluish-green colour.	do.	do.	Pp. Green colour.	Pinkish colour.	do.	Pinkish-yellow colour.	Pp. turning reddish.
Spanish oak (<i>Q. falcata</i>)	Green pp. and pp.	do.	do.	Pp. Red-brown pp.	Yellow colour, some pink.	do.	Yellow with pink streaks.	do.
White oak (<i>Q. alba</i>)	do.	do.	do.	Pp. Brown-green colour.	Pinkish colour.	do.	Pinkish colour.	Pp. turning pink.
Willow oak (<i>Q. phellos</i>).	do.	do.	do.	Pp. Red-brown pp.	Very yellow colour.	do.	Yellow with pink streaks.	Pp. turning green, liquid reddish.
Chestnut oak (<i>Q. prinus</i>)	do.	do.	do.	Pp. Red-brown pp.	do.	do.	do.	Pp. turning pink.
Swamp white oak (<i>Q. bicolor</i>).	do.	do.	do.	No pp. Greenish-brown colour.	do.	do.	do.	Pp. turning green, liquid reddish.
English oak (<i>Q. robur</i>).	Bluish-green colour.	do.	do.	..	do.	do.	do.	Pp. turning pink.
Indian oak (<i>Q. semicarpifolia</i>).	Green pp. and pp.	do.	Pink colour, changing to brown pp. Brownish-yellow pp.	Pp. Red-brown pp.	Decided pink colour.	do.	Pink colour.	do.
				..	Pink colour.	do.	Yellow colour.	do.

* See p. 146.

The following table is given by Andreasch * for alcoholic solutions, and has been found useful at the Vienna Institute for the examination of alcoholic extracts of leathers. The reagents

Reagent.	Spruce Bark.	Oak Bark.	Willow Bark.	Mimosa Bark.	Hemlock Bark.	•Oakw
Water	Orange turbidity.	Yellow-white pp., partly soluble.	Greenish turbidity.	Yellow-white pp., brown solution.	Dark red-brown pp.	Light y turbid
Hydrogen peroxide.	As above.	Yellow-white pp., partly soluble.	Apple-green pp.	As above.	Light brown pp. and soln.	Yellowish flocculer
Hydrochloric acid.	Red-brown solution.	Yellow-brown pp., brown solution.	Yellow-white pp., rose-red zone.	As above.	Dark brown pp. and solution.	Pale l flocculer
Sulphuric acid.	Rust-brown pp. and solution.	Yellow-white pp., brown solution.	Yellow-brown pp., cherry-red zone.	Slight rust-brown pp., dark solution.	Dark rust-brown solution.	Brown p soluti
Nitric acid	Yellow-brown pp., dark brown solution.	As above.	Yellow pp. and solution.	As above.	Red-brown pp. and solution.	Yellow flocculer
Acetic acid	Yellowish white pp.
Ammonia	Brown pp., partly soluble in excess.	Dark yellow pp., soluble in excess.	Turbidity.	Violet-red pp., soluble in excess.	Dark brown pp., insoluble in excess.	Pp. solul red soluti excess
Chloroform	Yellow-red flocculent pp., brown solution.	Yellow-white pp., yellowish solution.	Whitish turbidity.	Dark br deposi
Diethyl-ether	Light brown pp.	Light yellow pp	..	Grey-violet pp.	Brown pp.	Slightly yellow white l
Acetic ether	Turbidity
Anisole	Reddish-brown sediment.	Brown flocculent pp.	..	Reddish-black layer below.	Brown layer below.	Slight r brown l
Diethyl-ether	Ether not coloured.	Ether pale yellow.	Ether faint red.	..
Carbon disulphide.	CS ₂ yellow.	CS ₂ yellow.	CS ₂ green.	CS ₂ pale yellow.
Naphthol	Brown pp. and solution.	Brown pp. and solution.	Yellow-brown pp., dark red-brown solution.	Brown pp. and solution.	..	Yellow-bi pp., da solution
Glycerin	Yellow flocculent pp.	..	Greenish-white flocculent pp.	..	Red flocculent pp.	Slight turbidit
Asiatic acid	Whitish-yellow turbidity.	Slight whitish-yellow pp.	Yellow-green flocks.	Yellow-brown pp.	Red-brown pp.	Whitish-yellow flocculent
Nitric acid	As above.	As above.	As above.	As above.	As above.	As above
Sulphuric acid	As above.	As above.	As above.	As above.	Voluminous red-brown pp.	As above
Diethyl-phenol	Yellow pp. and solution.	Yellow-brown pp.	..

* Gerber, 1894, pp. 195, 207.

were always added in excess, and the mixture allowed to stand overnight. Where spaces are left blank it is understood that no visible change takes place.

Quebracho.	Valonia.	Myrobalans.	Divi-divi.	Sumach.	Knopperr.	Birch
Turbidity.	Dirty yellow, turbid over dark zone.	Dirty yellow turbidity.	Marked yellow-brown turbidity.	Dirty green pp.	Yellow white pp.	Yellow turbid
Brown yellow flocculent pp.	As above.	Yellowish pp.	Yellowish pp.	Green pp.	As above.	Rusty pp
As above.	Light brown turbidity.	Light brown turbidity.	Whitish-yellow pp.	Dark green pp.	As above.	Yellow pp
Dark red solution.	Slight yellow pp., pale solution.	Slight yellow-brown turbidity.	Dirty reddish pp.	Light green pp., green solution.	Yellow-grey pp.	Dense brown dark sol
Slight pp., red brown solution.	Slight pale pp., dark solution.	Dull red coloration.	Dirty brown turbidity	Dark green pp.	Dark yellow pp.	Red-brown and sol
..	Yellowish turbidity.	Dark yellow turbidity.	Light brown turbidity.	Dull dark green pp.	Yellow-brown pp.	..
Dark red-brown pp.	Yellowish pp., partly soluble, reddens.	Yellowish pp., turns brown, soln. in excess.	Pale yellow pp., partially soluble in excess, turns brown.	Pale green pp., darkens.	Dense greyish-white pp., reddening.	Dark fls pp., solu excess
Solution pale yellow, above red-brown.	Yellow-grey flocks.	Yellow flocks.	Yellow-brown flocks.	Slight green deposit.	Dense yellow-white pp.	Slight br pp.
..	Grey-brown pp.	Trace of coloured
..	Dirty white pp., turning dark brown.	Pale yellow flocks.	Rust-brown pp.	Slight yellow pp. on long standing.	Reddish-yellow flocks.	..
..	Ether yellow-green.	..
..	Dense yellow flocks at zone.	CS ₂ scarcely coloured, yellow flocks at zone.	CS ₂ scarcely coloured, yellow flocks at zone.	CS ₂ coloured green.	CS ₂ coloured yellow-green.	..
Yellow-brown pp., dark solution.	Slight yellow-brown pp.	Slight yellow-brown pp.	Slight yellow-brown pp.	Green-brown pp.	Slight greyish pp. on long standing.	Yellow-b pp., dark solutio
..	Long standing yellowish pp.	Long standing yellow flocks.	Long standing slight turbidity.	Long standing dark green pp.	Slight turbidity.	Turbid
Yellow-brown flocculent pp., dark red soln.	Yellow-grey pp.	Yellowish pp.	Yellowish pp.	Greenish pp.	Yellow-green pp.	Light re brown
As above.	As above.	As above.	As above.	As above.	As above.	As above
As above.	Sulphur yellow pp.	As above.	Yellow-brown pp.	As above.	As above.	As above
..	Brown-yellow pp., turns lemon.	Yellow-brown pp. turns yellow.	Turbidity first reddish, then yellow.	Apple-green pp.

TABLE FOR ALCOHOL

Reagent.	Spruce Bark.	Oak Bark.	Willow Bark.	Mimosa bark.	Hemlock Bark.	Oakwood.
Salicylic acid.	Light-brown pp.	Yellow-white flocculent pp.	Greenish-yellow pp.	Slight brown pp.	Bulky red-brown pp.	Yellow-white pp.
Tartar emetic.	Fawn-coloured pp.	Greyish-yellow pp.	Greenish-white pp., deep green layer above.	Violet-red pp.	Dirty brown pp.	As above.
Potassium ferro-cyanide.	Yellow-white pp.	Yellow-white pp.	Green white pp.	Flesh-red pp.	Red-brown pp.	Slight white pp.
Potassium sulphocyanide.	Yellow-brown flocculent pp. sol. on heating.	Yellow-brown flocculent pp.	Leaf-green pp.	Chocolate pp.	Red-brown pp. sol. on heating.	Yellow-white pp., pale yellow solution.
Potassium cyanide.	Pale-brown turbidity.	Pale-brown turbidity.	Leaf-green pp., yellowish sol.	..	As above.	Pp. brown below, yellow-white above.
Lime . . .	Yellow-brown pp., glittering on surface.	Pp. yellow-brown below, chocolate above, yellow solution.	Dirty sulphur-yellow pp.	Violet-blue pp., brown above.	Violet-brown pp., dull brown and glittering above.	Pp. white below, above blue, later brown.
Baryta . .	Dirty yellow pp., yellow-white solution.	As above.	As above.	Blue-green pp., brown above.	As above.	Blue pp. turning brown, glittering red-brown above.
Strontian .	As above.	As above.	As above.	Dirty blue pp.	As above.	Pp. white below, blue above, turning brown.
Magnesia .	Light-brown pp.	Dirty white pp.	Violet-red pp., green solution.	Grey pp.	Red pp.	Yellow-white pp.
Potassium chromate.	Dull brown pp.	Yellow-brown pp.	Bright yellow pp.	Brown pp.	Brown pp.	Green-brown pp., turning brown.
Mercuric chloride.	Light red brown pp.	Yellow-white turbidity.	White pp.	Light reddish-blue pp.	Blood-red pp.	Yellow-white flocculent pp.
Mercurous nitrate.	Dirty grey-brown pp.	Pp. reddish yellow turning brown.	Dirty yellow pp. on long standing.	Dirty brown pp.	Red-brown pp., turning dull brown.	Brick-red pp. turning brown-red or yellow.

SOLUTIONS—continued.

Quebracho.	Valonia.	Myrobalans.	Divi-divi.	Sumach.	Knoppern.	Birch Bark.
Brownish yellow pp., dark red-brown liquid.	Greyish-yellow pp.	Yellowish pp.	Yellow-brown pp.	Green pp.	Greyish-yellow pp.	Pale rust-brown pp.
Fawn-coloured pp.	Pale grey-yellow pp.	Cream-coloured pp.	Ochre-yellow curdy pp.	Yellow-green curdy pp.	Dirty white curdy pp.	Bulky pale rusty pp.
Pale red-brown pp.	Pale yellow pp.	Cream-yellow pp.	Orange pp.	Pale-green pp.	Yellow-green pp.	Bulky pale rusty pp.
..	Yellow-grey pp.	Yellow pp.	Dark yellow pp.	Green pp.	Orange yellow pp.	Turbidity.
Slight pp. amaranth-red solution.	As above.	As above.	As above.	As above.	Curdy reddish-white pp., darkens on standing.	Yellow-white pp., dull brown and glittering above.
Violet-brown pp., dark brown above.	Pale chocolate pp.	Bright yellow pp., colourless solution.	Cream-coloured pp., which darkens.	Green pp., turning yellow.	Olive-brown pp.	Flesh-red or scarlet pp.
Grey-white pp., glittering chocolate-brown above.	As above.	As above.	As above.	Green pp., turning sulphur-yellow.	Green pp., turning grey-brown overnight.	Grey-white pp., brown above.
As above.	Chocolate pp., turning black.	Dirty green pp., turning brown.	Pale red pp., dirty grey above.	As above.	As above.	Greyish-white pp., vermillion above.
Violet pp., dark solution.	Yellowish pp.	Yellowish pp.	Grey-brown pp.	Dirty green mass.	Yellow-white pp.	Pale flesh col. pp.
Dark, dull brown pp.	Yellow-brown pp.	Dirty brown pp.	Dark-brown pp.	Dirty brown pp.	Dark red-violet pp., turning chocolate.	Chestnut-brown pp.
Dark turbidity.	Dirty yellow pp., partly soluble.	Yellow-brown pp. solution in excess.	Brown pp., mostly sol. in excess.	Dirty green pp., part soluble in excess, turns yellow.	Yellow-green pp.	Reddish-yellow pp.
Chocolate pp. on long standing.	Orange-yellow pp., turning dirty grey.	Orange-yellow pp., turning dirty yellow.	Orange yellow pp., turning dirty yellow.	Grass-green pp.	Orange pp., turning grey.	Grey pp.

SECTION X.

ANALYSIS OF TANNING MATERIALS. HISTORICAL NOTICE.

THERE are few organic determinations which have been the objects of more varied suggestions and proposed methods than the estimation of tanning matters, and unfortunately it cannot be said that the problem is yet solved in a wholly satisfactory manner, although, for commercial purposes, the present methods have proved extremely useful. Of the many proposed, only those depending on the indirect weighing of the tannins absorbed by hide, and on its volumetric estimation with an oxidising solution of permanganate in presence of indigo, have held their own as practicable, accurate and suitable for general use under the test of experience, and in most cases the indirect gravimetric method is to be preferred to every other, though there are exceptions for which the permanganate volumetric method is still useful.

Before proceeding to describe the modern methods in detail, a short sketch of earlier processes is desirable, if only to save younger chemists the labour of re-inventing what has already been tried without success.

Taking first the methods dependent on precipitation: the oldest is that of Sir H. Davy,* which has been somewhat improved by Stoddart and others, and which consists in precipitating with gelatin, and drying and weighing the precipitate. This, with many materials, is almost impossible to filter off as directed by Davy; but by the use of a little alum, and by pouring hot water on the precipitate, the latter becomes curdled into a mass which may be washed by decantation. As the precipitate contains varying quantities of tannin, according to the strength of solution employed and the amount of washing it has received; as it is soluble in excess of gelatin solution, and almost if not quite impossible to wash free from uncombined gelatin and alum, the method can hardly lay claim to much accuracy. A some-

* Phil. Trans., xciii. p. 233.

what better one (Warrington, Müller) depends on employing a standard solution of gelatin with a little alum, and determining the end of the reaction by filtering off a portion of the tanning solution, and ascertaining if another drop of the reagent produces a further precipitate. This method is very tedious, the end reaction is difficult to hit, especially as the neutral solution gives precipitates with *both* gelatin and tannin; the standard solution is very unstable, it is inapplicable to many materials, and especially to gambier and cutch, because the mixture will not filter clear, and its results are irregular, probably from the power of tannin to combine with various proportions of gelatin. Saturating the solutions with ammonium chloride gives in some cases somewhat better results. Attempts to use basic aniline colours (which are also precipitated by tannins) as indicators, by adding them to the gelatin solution, have failed from the fact that, on the one hand, the precipitation is with many tannins imperfect, and on the other, that the colour is absorbed by the precipitated gelatin tannate. Some tannins can be fairly estimated by precipitation with a standard solution of a basic colour such as benzaldehyde green in presence of sodium acetate, but the method is not of general applicability nor very satisfactory, and at best is rather adapted to the dyer than the tanner.

The tannins are precipitated by most alkaloids, and Wagner * employed a standard solution of cinchonine sulphate coloured with rosaniline acetate as indicator, but the results proved much too low, and quite unreliable.

Messrs. Trotman and Hackford † have recently proposed a direct gravimetric method for the analysis of tanning materials, in which extraction is made with alcohol in an electrically heated Soxhlet apparatus, the partially evaporated extract being diluted with water, the resinous matters filtered off, and tannin estimated in the filtrate. 25 c.c. of this is placed in a 250 c.c. flask and diluted somewhat with water. 0.25 grm. of strychnine is then weighed out and dissolved in about 50 c.c. alcohol. To this an equal volume of water is added, the mixture cooled and added to the tannin infusion, the contents of the flask being diluted to the mark and thoroughly mixed. The precipitate is collected in a weighed Gooch crucible, dried first in air, and then in the vacuum oven. Gallotannic acid and sumachs yield

* Zeit. Anal. Chem., v. p. 1.

† Journ. Soc. Ch. Ind., 1905, p. 1098.

good results, a definite compound, $C_{21}H_{22}N_2O_2 \cdot C_{14}H_{10}O_6$ (strychnine tannate) being obtained for weighing.* With most tanning materials, however, lower results are obtained than by the hide powder method, much lower indeed than can possibly be accounted for by the non-estimation of astringent non-tannins, showing clearly that all tannins are not precipitated by strychnine. On the other hand, the fairly high results obtained with materials containing no gallotannic acid show that some other tannins can be estimated in this way.

Messrs. Payne and Parker have also worked volumetrically with morphine, brucine, and some of the artificial aromatic bases with some success. Many metallic salts have also been used as precipitants, both gravimetrically and volumetrically, but in most cases without satisfactory result, because either the precipitation was incomplete, or other substances, such as gallic acid and colouring matters, were carried down with the tannins.

A further difficulty arises in all these methods from the fact that the tannins form a class with very considerable chemical diversity, and that therefore methods which give accurate results with one tannin, either fail to act, or give quite different results when applied to another. It is, indeed, a universal fault of these methods that even if for one tannin the results are constant, no direct comparison is possible between materials containing tannins of different classes. This difficulty is to a large extent overcome by the gravimetric hide-powder method, which gives the actual weight of any tannin absorbed by hide, and thus allows of at least approximate comparison of the tanning value of totally dissimilar materials.

Among the processes based on the precipitation with metallic salts which gave useful results must be mentioned that of Gerland,* in which a solution of antimony potassium tartrate is used in conjunction with ammonium chloride, to assist the settling of the tannin precipitate and prevent the co-precipitation of gallic acid. The process was improved by Richards and Palmer,† who substituted ammonium acetate for the chloride, adding 4 per cent. of a concentrated solution of the salt to the tannin solution, and employing 6.730 grm. per liter of the antimony potassium tartrate (previously dried at 100°C.), of

* Chem. News, viii. p. 54.

† Amer. Journ. Science and Arts (3), xvi. pp. 196, 361.

which solution 1 c.c. corresponds to 0.01 grm. of digallic acid. The end of the reaction is determined by adding a drop of sodium thiosulphate solution to a little of the clear supernatant liquid placed on a white tile, and warming when the formation of red antimony sulphide indicates the least excess of the reagent. The method gives good results with sumachs and other materials containing gallotannic acid, but is somewhat tedious, and does not act well with many catechol-tannins. The tartar emetic solution is apt to be spoiled by fungi, and keeps better if an antiseptic, such as phenol or a trace of mercuric chloride, be added. Copper acetate,* with subsequent addition of ammonium carbonate to remove gallic acid, also gives fair results gravimetrically with gallotannic acid and some other tannins, but it is not applicable to the large class (see p. 158) of which the cupric salts are soluble in ammonia. This criticism also applies to the use of copper salts suggested by Darton to remove tannin for estimation by the permanganate process, which will be alluded to later, since in particular cases it enables the proportions of different tannins to be determined quantitatively in mixture.

The use of ammoniacal solutions of zinc for the same purpose by Carpené † and others was carefully examined by Kathreiner, ‡ but without satisfactory results.

Another class of methods is based on the amount of some oxidising substance required to destroy the tannin present. The simplest of these in theory is that of Mittenzwey and Terreil, in which a solution of tannin, rendered alkaline with caustic potash or soda, is allowed to absorb oxygen from a known quantity of air, the loss in volume of which is measured. § The absorption is slow, and the method difficult to carry out, and subject to several sources of error. In a more recent modification || the oxygen is furnished by a known quantity of hydrogen peroxide acted upon by lead peroxide in alkaline solution, but this appears to have no important advantage over the original method. Vaubel and Scheurer ¶ suggest modified apparatus,

* H. Fleck, *Bay. Kunst und Gew. Blatt*, 1860, p. 209.

† *Ding. Polyt. Journ.*, 1875 (816), p. 452; 1876 (219), p. 471.

‡ *Ding. Polyt. Journ.*, 1878 (227), p. 481.

§ Mittenzwey, *Journ. f. Prakt. Chem.*, ii. (1864) p. 815; Terreil, *Compt. Rend.*, lxxviii. (1874) p. 990.

|| A. Thompson, *Compt. Rend.*, 1902 (cxxxv.), pp. 689-691; *Colleg.*, 1902, p. 334.

¶ *Colleg.*, 1907, p. 96.

and give interesting test analyses, but admit that the method is not ripe for practical adoption. None of these methods make any distinction between tannins and other astringent products which do not tan, such as gallic acid, so that a second estimation must be made after removal of the tannin, and the latter determined by difference. Commaille* oxidised with a known quantity of iodic acid in presence of a trace of hydrocyanic acid, and determined the excess of undecomposed iodate. The process was troublesome, not very exact, and, like all other oxidation processes, involved a separate estimation of gallic acid. The power of iodine to enter into combination with tannin has also been utilised by F. Jean,† who uses a standard solution of iodine, which is titrated with the tannin solution rendered alkaline by sodium carbonate. As the colour of the mixture is too dark to allow of the starch reaction being seen in the usual way, minute drops are brought in contact with a piece of filter paper rubbed with starch. The method gives fair results with some tannins, but does not distinguish gallic acid from tannin (see p. 230).

The use of potassium permanganate for the estimation of tannins was first proposed by Monier,‡ but is not practicable in the simple form of direct addition by permanganate, from the fact that the reaction proceeds very slowly, and in the cold never reaches its theoretical limit. Gantter§ has since shown that it is possible to obtain useful results by titrating in boiling solution by a method which does not differ in principle from Monier's. The original method of Löwenthal|| introduced the valuable improvement of adding indigo solution to the tannin solution to be titrated; the indigo acting not only as an indicator, but controlling the oxidation of the tannin within certain definite limits. Löwenthal first assumed that only tannins were attacked, but as gallic acid is also similarly oxidised by permanganate, a double titration was found to be required where both were present, the tannin being removed in the second

* Compt. Rend., lix. p. 398.

† Ibid., lxxii. p. 982; Berichte Deut. Ch. Ges., 1877, p. 430.

‡ Compt. Rend., 1858, p. 577.

§ Zeits. für Angew. Chem., 1889, p. 20; cp. also Procter, Journ. Soc. Ch. Ind., 1890, p. 260.

|| Journ. Prakt. Chem., iii. (1860) p. 150.

case, and several proposals have been made to effect this object; but from the time Löwenthal published his method of precipitating the tannin by gelatin in the presence of an acidified salt solution,* to the introduction in 1886 of the indirect gravimetric hide-powder method, scarcely any other method than this, with removal of tannin either with gelatin or hide-powder, was in practical use for the estimation of tannin, and in certain cases it is yet the best available.

The "indirect gravimetric method" first took practical form at the Vienna Research Station for Leather Industry, and was published in its organ 'Der Gerber'† by F. Simand and B. Weiss, who first applied it to extracts only, but afterwards, in conjunction with Eitner and Meerkatz,‡ described its application to solid materials. Earlier methods, which to some extent involved the same principles, were those of Hammer§ and Müntz and Ramspacher.|| In the former of these the specific gravity of a dilute tanning infusion was taken with a very delicate pycnometer or areometer before and after the tanning matter had been removed by hide-powder. A special table gave the amount of gallotannic acid which corresponded to the difference of specific gravity, according to which 1 per cent. solution of gallotannic acid has a specific gravity of 1.0040 at 15° C.; and as at least up to 5 per cent. specific gravity is proportional to the quantity of tannin, the percentage may be obtained by dividing the decimals of the specific gravity by 0.004. Extreme accuracy in taking the specific gravity and in the temperature of the solution is required to obtain even approximate results, and determinations are still wanting of the specific gravity of solutions of other tannins than gallotannic acid. In Müntz and Ramspacher's method the liquid was detannised by filtering under pressure through a piece of raw hide, and the tannin determined either as in Hammer's method, or by evaporation. The weak point of the method is that if sufficient of the tannin infusion is passed through the hide to insure the expulsion of the water contained in it, the liquid is rarely completely freed from tannin. In

* Zeit. Anal. Chem., 1877, pp. 33 and 201; see also p. 223.

† 'Gerber,' xii. (1886), pp. 1, 26, 35; Ding. Polyt. Journ., cclx. p. 564.

‡ 'Gerber,' xlii. (1887), p. 2.

§ Ding. Polyt. Journ., xlix. p. 300.

|| Compt. Rend., lxxix. p. 300.

experiments by the author the results, even with the greatest care, varied for the same liquor by 10 per cent. of the total tannin present.

Simand and Weiss's method was originally carried out as follows: The "total soluble" in a clear filtered, solution of the extract was determined by evaporation of 100 c.c. of the solution to dryness in a platinum basin, and subsequent drying at 100°C., the solution being of such strength that this residue amounted to 1.0-1.2 gm. 250 c.c. of the same solution was treated in a dry conical flask with 1 gm. of the dry purified hide-powder, and allowed to digest for several hours in a cool place, during which it was frequently and vigorously shaken. It was then filtered through linen, 2 gm. more of the hide-powder added, and the digestion continued for 12-16 hours more, when a further 2 gm. of the powder was added and similarly digested. At the end of this time the liquid was filtered through paper, and 100 c.c. of the perfectly clear filtrate evaporated. The residue consisted of "soluble non-tanning matter," and when deducted from the "total soluble," left "tanning matter absorbed by hide." If the whole powder were added at once to a comparatively strong tanning solution, the surface would become tanned and no longer capable of rapidly absorbing small traces of tannin. By adding the powder successively, the greater part of the tannin is absorbed by the first portions of powder, leaving only traces to be absorbed by the last addition. With carefully purified hide-powder, free from soluble matter, the method is capable of giving good results, but is surpassed by more recent modifications.

Soon after Simand and Weiss's publication, it occurred to the writer* (suggested, perhaps, by Müntz and Ramspacher's method) that the determination might be still more rapidly effected by the use of a cylindrical filter packed with hide-powder, through which the tannin liquor was slowly percolated, so that most of the tannin should be absorbed by the first portions of the filter traversed. This method was at once adopted by the Vienna Research Institute, with some improvement in the form of the filter,† and continued to be the standard method of the International Association of Leather Trades Chemists up to the present year (cp. p. 211).

* Journ. Soc. Chem. Ind., 1887, p. 94.

† 'Gerber,' 1887, p. 65.

More recently a method has been published,* by Dr. Yocum, which reverted to Simand and Weiss's original system, but shortened the digestion required to about ten minutes by vigorous mechanical shaking. The results agree very closely with those of the filter, but are generally somewhat lower in tannin. With some tanning materials, and especially with gambiers, the differences are considerable. This method with modifications was adopted by the American Association of Official Agricultural Chemists, but has been superseded by that described on p. 216, as it was found so difficult to prepare a pure hide-powder of constant absorptive power and really free from soluble organic matters, that many chemists have turned their attention to the use of powders made insoluble by the use of chrome salts, and in one form or another these have been generally adopted. Powders made insoluble with formaldehyde have also been tried, but apparently become unabsorptive on keeping.

No historical notice of methods of tannin estimation would be complete without allusion to that recently introduced by Parker and Payne† and dependent upon an estimation of the total acidity of the tanning infusion with lime or baryta solution by a method not dissimilar in principle to the determination of the saponification value of a fat (p. 304). The process has not proved wholly satisfactory, but the special information which it aims at giving is so important that it is described in some detail in Section XIV.

The work of Prof. Wislicenus‡ with "fibroid alumina" must also be referred to, since, although in the writer's opinion it is not likely to replace the use of hide-powder, it presents certain advantages which would have entitled it to very favourable consideration had the hide-powder methods not been previously established in technical use. When metallic aluminium is moistened with a mercuric salt, such as mercuric chloride, metallic mercury is reduced, and a galvanic couple is produced, which, under the influence of the air and moisture, oxidises the metal to alumina, which appears as a sort of down on the surface, of a fibrous nature, and remarkably like a growth of some form of

* 'Leather Manufacturer,' 1894, No. 9; Journ. Soc. Chem. Ind., 1894, p. 494.

† Journ. Soc. Ch. Ind., 1904, p. 648.

‡ Collegium, 1904, pp. 204, 215, 223, 225; 1905, pp. 85, 94, 213, 230; 1906, pp. 77, 87, 316, 321; 1907, pp. 157, 169; Zeits. für Angew. Ch., 1904, No. 25; Zeits. für Anal. Ch., No. 2.

mould. This constitutes the "sprouted," or "fibroid" alumina, which is employed by Wislicenus as substitute for hide-powder, and which, from its considerable adsorptive power and large surface, is capable of taking up from solution all tannins, and many of the substances which are usually classed as non-tanning. In the first instance, considerable difficulty was experienced in producing this material of constant and reliable quality; but detailed instructions have been given by Wislicenus, and the powder is now to be obtained of satisfactory quality from Merck. It has the advantage over hide-powder that it can be used repeatedly, the carbon being destroyed by heating to something below the point of redness; but strong ignition lessens or destroys the adsorptive powers. Being also entirely combustible and inorganic, it is possible to determine the organic substances absorbed by it by elementary analysis of the powder after use. The substance is employed in a filter-tube, which, owing to the smaller quantity, only 2.5 grm. employed, has been considerably modified from the form used for hide-powder, and in its latest development is described in *Collegium*, 1907, p. 172. The results obtained show good concordance in themselves, and do not differ very largely from those with chromed hide-powder, but the absorption is commonly somewhat greater and the non-tannins consequently lower. It is also by no means certain that the selective absorption of the alumina is for the same "non-tannin" substances as that of hide-powder, since its adsorption is mainly a surface action, while in the case of hide-powder there is little doubt that chemical affinities also come into play. It may be mentioned that instead of the candle-filter, Prof. Wislicenus prefers to use a perforated porcelain tube, covered with several thicknesses of filter paper, for preparing his solutions.

A method mentioned by Dr. Baum* at the Frankfort Conference of 1906, but not since further described, depends on somewhat similar principles to that of Prof. Wislicenus. The tannin solution to be detannised is placed in an aluminium basin and submitted to electrolysis with a current of low voltage, the tannin being precipitated in combination with alumina.

* *Collegium*, 1906, p. 373.

SECTION XI.

SAMPLING, GRINDING AND EXTRACTION OF TANNING MATERIALS.

BEFORE proceeding to describe the practical analysis of tanning materials, careful consideration must be given to the drawing and grinding of samples, and the extraction of the tanning matter in a proper form for analysis, as in many cases greater errors arise in these preliminary operations than in the analysis itself. In the case of extracts, samples should be drawn by a sampling tube by which a portion of extract can be withdrawn from 6-10 casks of the parcel to be analysed. These portions are carefully mixed, and 4-6 oz. at least transferred to a clean bottle. A suitable sampling tube is designed and sold by Mr. Arthur Priestman, of 275 Burlington Street, Liverpool, consisting of a small reservoir closed by a valve operated by a rod passing through a long tubular handle. Before sampling, the extract should be thoroughly stirred and mixed by the sampling tool, special care being taken to disturb any sediment which has settled to the bottom of the cask. If the extract has been standing in cask for some time, the only way really to mix properly is to take out the heads of a sufficient number of casks, and stir the contents thoroughly with a suitable stirrer or paddle, rolling full casks being quite ineffective. After thorough mixing, the tool is immersed and moved about in the cask, while the reservoir is filled by depressing the rod which passes down the handle, and which opens an aperture for the purpose. Samples should be drawn not only from the centre but also from the upper and lower corners of the cask. The various samples should be thoroughly mixed in a clean pail, and at once sealed in bottles for analysis. It is desirable, if the casks are numbered, to select for sampling, numbers equally distributed through the parcel, as the casks are usually filled in rotation. It is also of equal importance that samples in bottles or jars should be thoroughly mixed before weighing out portions for analysis, as Dr. Parker has shown * that errors of 2 per cent. in

* *Leather Trades Circular*, 1897, p. 489.

either direction may be caused through the settling of the "difficultly soluble tannins."

The sampling of block gambiers is one of the most difficult problems owing to the irregularity of the moisture in different parts of the block. A somewhat large sample must be drawn either by perforating the blocks with a tubular sampling tool like a large cork borer,* or by cutting sections with a "fleshing knife," and the portions must be mixed by chopping or kneading, with as little exposure to the air as possible to avoid loss of moisture. Similar difficulties with regard to moisture often

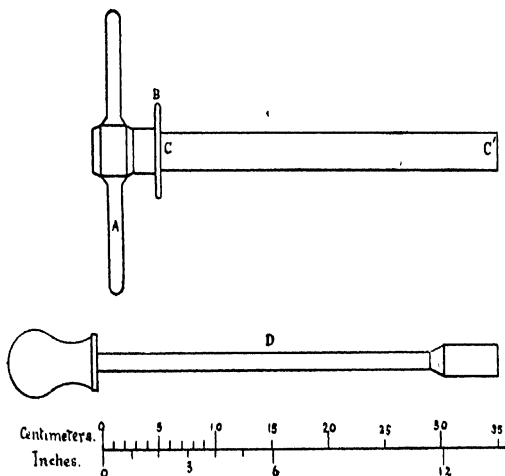


FIG. 9.

arise with cutch and other solid extracts, which are usually too hard and brittle to cut with the tool, and cannot be pulverised till dry. In this case it is best to weigh the whole sample, dry, and again weigh to determine loss. The sample is then pulverised and analysed in the usual way, and calculated to original moisture. An example of the reckoning may be given. The original sample weighs 900 grm. and after drying 765 grm. only,

* A suitable tool, designed by Kathreiner, is shown in Fig. 9, which can also be used for sampling sumach, if damage to the bags is not objected to. C C' is a brass or gunmetal tube with a collar B and strong handle A. The plunger D is of hard wood, and used to force the 'cores' cut out of the cutting tube.

the loss being 15 per cent. The percentage is therefore calculated on 85 as representing 100 original, and 15 per cent. is added to the water.

In sampling solid materials, portions should always be drawn from at least ten sacks or separate parts of the bulk, and, in the case of valonia, special care should be taken to have a fair average quantity of "beard." No attention is usually paid to this point by merchants, and the proportion varies greatly in different parts of the same cargo. If several sacks are spread in layers on a level floor, and then "quartered," dividing the pile first in half, and the half again in halves, till a sufficiently small sample is obtained, this will be accomplished. Where samples must be dealt with which have not been specially drawn, it is safest to weigh out from the same proportion of beard and whole cups, bearing in mind that the beard is always the richest part of the valonia; or to make the analysis on the cups only. Valonia beard often contains large quantities of crushed lime-stone and other rubbish added as weighting material, but frequently very injurious to the colour of leather. Special care is required in sampling and mixing sumach, as it is very frequently adulterated, and probably a portion of pure is often added on the top of the sack. In sampling myrobalans, it should be remembered that the poor and light nuts will rise to the top, and hence the hand should be plunged well into the sack. The sample, when drawn, may be ground in a small bark-mill, and, if necessary, a smaller sample drawn from this and ground a second time in a sample mill, or even an ordinary coffee-mill, though the latter is scarcely strong enough for many materials. Burroughs, Wellcome and Co.'s drug mills, No. 3 or 4, answer the purpose very fairly. A special mill of small size is also sold under the name of "Tannina" by Robert Paessler, of Freiberg, Saxony, and small sizes of the ordinary toothed grinding mills for tanning materials, such as Schmeijja's, Gläser's, or the Hardy Pick Co.'s may also be used, especially if power is available. A laboratory disintegrator is made by Grumbach and Son, of Freiberg in Saxony, to a design of Dr. Koerner's.* If a suitable mill is not at hand to reduce the material to a coarse powder, it is necessary to prepare it for these small mills by crushing or breaking into pieces of moderate size. With many

* Collegium, 1903, p. 365.

materials this is conveniently accomplished with a flat-faced hammer on a thick cast-iron plate, which should have raised ledges round three of its sides to prevent the fragments from flying about. Many barks are too tough to be pulverised in this way, and are most easily sampled by cutting short lengths off a large number of pieces with strong shears, or with a saw. If the bark can be secured in a firm bundle with a clamp or by binding with wire, a number of thicknesses may be cut at once with the saw. Materials are usually much more easily ground if strongly dried, but this involves determination of the moisture both on a portion of the original sample, and again on the dried and ground material as prepared for analysis, and should therefore be avoided if possible.

Extraction.—Extracts are most satisfactorily dissolved for analysis by placing the beaker or basin in which they are weighed in a large funnel in the neck of a liter flask, and washing the extract into the flask with boiling water. After filling up with boiling water the neck of the flask is then covered with a small beaker, and the liquid cooled rapidly under a stream of water from the tap, and made up to the mark with cold water.

If the tap water is much below 15°C . it is safer to immerse in a vessel of water at about that temperature, to avoid over-cooling or local chilling of the solution. Solid extracts are generally best dissolved in a beaker by the use of successive quantities of boiling water, and treated in the same way. Care must be taken not to pour solid particles into the flask until all matter soluble in hot water has been dissolved, and if it is suspected that solution is not complete, the flask may safely be heated for a short time on the water-bath. If the amount of insoluble particles is large, as in the case of some gambiers, it may be advisable to strain through muslin, or even to extract like a solid tanning material. A short boiling of the residue, after most of the tannin has been removed, is not generally injurious; but long-continued boiling of most tannin solutions, and especially in contact with air, leads to the destruction of some tanning matter, and almost invariably darkens the colour. The writer is of opinion that with most extracts slightly more uniform results are obtained by cooling at the temperature of the laboratory for some hours instead of rapidly under the tap, and this method has been adopted by the American Association

of Leather Chemists, but the results are somewhat lower in tannin and higher in insoluble matters; though experiment shows that the differences are negligible as compared to other sources of error; and in many cases want of time precludes the slower process, so that for the sake of uniformity it is considered best invariably to cool under the tap. For the same reason it is best, or at least official, to dissolve always in absolutely boiling water, for though many extracts dissolve perfectly well at lower temperatures, and sometimes filter more easily, in some cases the use of lower temperatures leads to a larger precipitation of insoluble "reds." It is pointed out by Mr. A. Barrett that loss is incurred with sumach extracts, and others containing ellagitanic acid, if *boiling* water is used, and better results are obtained with water not above 40°-50° C.

The insoluble matter found in an extract is considerably influenced by the quantity of water which is employed in dissolving it. This was long ago pointed out by von Schroeder, and is well shown by the following figures given by Cerych for an oak-wood extract: *

Dissolved per liter	Insoluble Matter.	Soluble Non-Tannins.	Tanning Substances.
gm.	gm.	gm.	gm.
5	0.12	18.44	28.56
15	1.22	18.50	27.40
30	1.65	18.40	27.07

• It will be noted that as the "insoluble" increases the tanning substances diminish, as the former consists largely of red anhydrides or "difficultly soluble tannins." In materials such as hemlock bark and quebracho, which contain these bodies in much larger proportion than oak-wood, the variation becomes still more marked. It is hence very important to keep to a uniform proportion of dissolved matter in the liquid for analysis in order to obtain comparable results, and this is one of the reasons why chemists interested in the analysis of tanning materials have agreed upon quantities to be adhered to (see p. 191), and Section XIII.

• The solubility of the "reds" is greatly influenced by tem-

* Gerber, 1895, p. 242.

perature, and consequently the quantity found will vary materially with the temperature at which the liquor is filtered for analysis. Cerych (*loc. cit.*) found that an oak-wood extract which gave 1.68 per cent. insoluble at 16° C. was perfectly soluble at 34° C. These remarks also apply to solid tanning materials. Tanning solutions for analysis should therefore be filtered at a temperature as little above 15° C. as possible, and never exceeding 20° C., even if artificial cooling is necessary.

The extraction of solid tanning materials presents much more difficulty than the solution of extracts. It has been pointed out by Mr. A. S. Jones that each tanning material has an *optimum* temperature of extraction, and that in many cases materially less tanning matter is extracted at a boil than at some less degree of heat, and considerable information on this point is given by the researches of Dr. Parker and the writer.* In many cases, also, it is difficult to complete extraction without the use of more water, and the consequent production of a more dilute solution than is permissible for the gravimetric method. As a rule, the digestion of the material for some hours at a low temperature or in the cold, and its subsequent percolation with water, of which the temperature is gradually increased to 100° C., will extract a maximum amount of tanning matter, and if all the concentration is done on the later dilute percolate, which contains at best a very small proportion of the total tannin, any loss by decomposition may be neglected. It is found, however, that in nearly every case by careful percolation practically the whole of the tannin can be extracted without exceeding the permissible volume of water, and this is now the rule of the I.A.L.T.C. (p. 213). Considerable difficulty arises from the tendency of many tanning materials to choke any filter on which they are placed for percolation, and this is on the whole most successfully met by the use of sand filters. One of the best appliances for the purpose is the bottle extractor devised by Dr. R. Koch,† which may be considered as an improvement and simplification of the so-called "Real's press." The apparatus (Fig. 10) consists of a glass wide-necked bottle which should be thin and well annealed in order to stand the heat of the water-bath. A convenient size is about 200 c.c. capacity. It is wise

* Journ. Soc. Ch. Ind., 1895, p. 635, and Prin. Leather Mfr., p. 344.

† Ding. Polyt. Journ., 1887, cxlvii. p. 513.

before use to heat these bottles in water to boiling, and allow them to cool in it, to lessen the risk of their cracking during an extraction, and it is often difficult to get bottles which will stand the test. The bottle is closed with a rubber cork, through which pass two glass tubes; one through which water is introduced extending about half an inch below the cork to prevent the cold water coming in direct contact with the heated sides of the bottle; while the other, which serves as an outflow, almost reaches

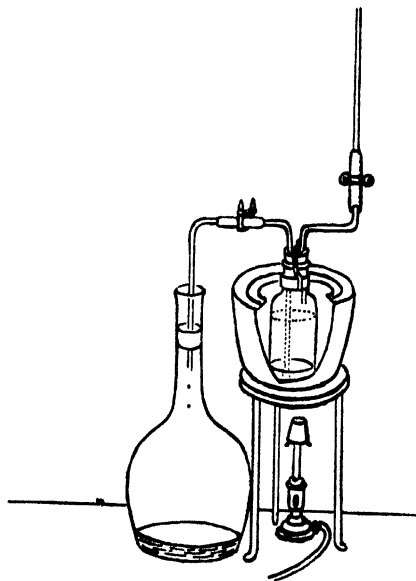


FIG. 10.

the bottom of the bottle, where it is widened to a funnel-shaped end, which in use is covered with a piece of the silk gauze used by millers. Above the cork both are bent at right angles for connection with other tubes. In use a layer of about 2 cm. of fine sand (purified by digestion with hydrochloric acid and washing), is first introduced into the bottle, and then the weighed quantity of ground tanning material. The funnel-tube and cork are now inserted, any slight disarrangement of the layers being of no consequence, as the sand speedily settles to the bottom on

filling the apparatus with water, which is done by sucking the short tube, while the funnel-tube is connected by a short length of rubber tube, with screw pinchcock, with a second tube bent at right angles and dipped in a beaker of water. The same tube afterwards serves to convey the percolate into a gauged flask. In special cases, where it is desired to obtain the extracted material free from foreign matter, the sand may sometimes be dispensed with. Where, from the fibrous character of the material, or other reasons, it is found difficult to insert the funnel-tube after filling the flask, it may be inserted first, and the flask filled by sliding the cork up the tube, and using a funnel for the sand and material.

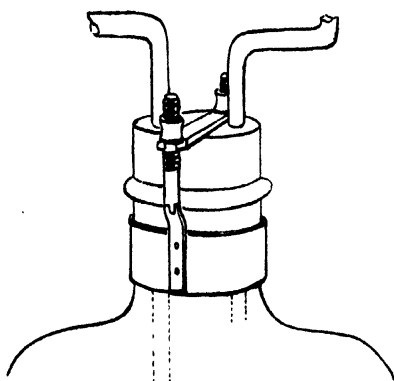


FIG. 11.

After filling, the cork is secured in the bottle, either by wiring like a champagne bottle, or by the special clamp shown in Fig. 11; the apparatus is placed in the water-bath, and the shorter tube is connected with a water supply about $1\frac{1}{2}$ meter above it by tubing, also provided with a screw pinchcock. The second tube is arranged to drop into a liter flask, as shown in the figure. The water-bath may now be gradually heated, and the percolation carried on at any desired temperature. If the gauze chokes, as is not unfrequently the case, it may sometimes be made to run, by sucking a little water backwards, as in filling the apparatus.

A slight modification of the Author's, which, together with

the Koch apparatus was accepted as official by the Turin Conference of the I.A.L.T.C., and which has the merit that it can be arranged from the apparatus found in every laboratory, is shown in Figs. 12 and 13 (from the catalogue of Messrs. Reynolds and Branson, of Leeds, who supply the apparatus). In place of a closed bottle, an ordinary open beaker is used, which is placed in a water-bath. A common thistle-head funnel is bent twice at right angles to form a syphon. The head, covered with silk gauze C, rests on the bottom of the beaker, the other end being lengthened by a piece of slender glass tube, connected by india-rubber tube fitted with a screw pinch-cock A, the

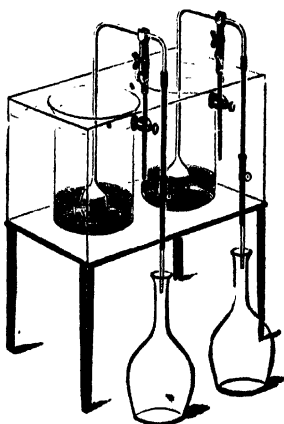


FIG. 12.

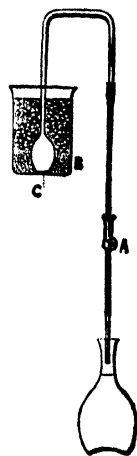


FIG. 13.

whole being held in position by a clamp. The beaker is filled with sand B and tanning material, as in Koch's apparatus, water is poured in, and the whole raised to the requisite temperature in the water-bath, when percolation is started by sucking, and warmed water added as required. As compared to Koch's, the apparatus has the advantage that, being open at the top, it can be stirred with a rod in event of the material clogging the filtering layer of sands, but on the other hand the beaker has to be watched and filled up as required, instead of having a supply cistern of a definite quantity of water which can be left to percolate automatically. In ordinary complete extrac-

tion in the Leeds University laboratory, the requisite quantity of material to give an extract containing 3·5-4·5 grm. of "tanning matter," see p. 191, per liter is weighed out into the apparatus, and allowed to macerate in water for some hours in the cold. The temperature is then gradually raised, and the percolation begun at about 50° C. About 500 c.c. is run through in 1-1½ hour, after which the temperature of the bath is rapidly raised to 100° C. In the case of sumachs, a good part of the first 500 c.c. should be percolated at or below 40° C., and with canaigre and other starchy materials the whole extraction is best done below 50° C.

The Turin Conference decided that only 1 liter should be used for extraction, and the small quantities of tannin which could be extracted with further portions of water should be neglected, but if solutions must be concentrated by evaporation, the boiling, if not done *in vacuo*, should be protected as much as possible from excess of air, by placing a funnel in the neck of the flask, and should be confined to the later and more dilute percolates.

After making up to 1 liter, the solution, whether of an extract or solid material, requires filtration, and for the sake of uniformity this is desirable even when the solution is quite clear and transparent.

In some cases it is very difficult to obtain such a filtrate, and special thick filter-paper is required, Schleicher and Schull's "No. 605 extra-hart" being very suitable. Even with this the patience of the operator is often severely taxed, as it is often necessary to return to filtrate again and again to the filter till absolute clearness is obtained. As a last resort, a teaspoonful of well-purified kaolin may be shaken up with the solution before filtration. It was early pointed out by von Schroeder that small traces of tannin are removed by the kaolin as well as by the filter paper itself, and many attempts have been made to overcome this source of error, which usually amounts to ½ per cent. or more on liquid extracts. A method of determining a correction was devised by the author, and adopted by the I.A.L.T.C. in their conference in 1902; given up in 1904 for the Berkefeld "filter-candle,"† but again accepted by the Tannin Analysis

† Collegium, 1902, pp. 119, 145, 151.

* Berkefeld Filter Company, Celle.

Commission of 1906 (see p. 213). The "candle" was first suggested by Kathreiner, but successfully introduced by Parker and Payne.* This filtering medium is very indifferent to tannins and other matters really in solution, and the filtrate is generally perfectly clear, but in some cases, especially with quebrachos, is slightly opalescent. For the sake of uniformity it was agreed by the conference of Turin, 1904, and by the commission it then appointed,† that all matter which has passed through the filter should be regarded as "soluble." It has, however, since been found that in some cases as much as 10 per cent. of matter will pass through the candle, which is removed by filtration to optical clearness. The "candle" adopted consists principally of porous infusorial siliceous earth and is about 7 cm. long, 3 cm. external, and 1 cm. internal diameter. Various methods of mounting have been suggested. Dr. Parker cements with shellac on a glass tube with a projecting collar, and fits with a rubber cork into a wide and deep ordinary funnel, which in turn is fitted with a rubber cork or collar into the neck of the usual vacuum filtration flask, from which the air is exhausted either by a water-pump or a syringe. The pumping must not be continuous, but as soon as the necessary vacuum is formed the connexion with the pump is closed with a pinchcock, to prevent loss by evaporation, and only opened if the vacuum becomes insufficient. Another, and, on the whole, preferable arrangement is to invert the candle in a narrow cylinder, connecting it by a syphon tube with the vacuum flask; in which case the tube should be prolonged to the bottom of the "candle," so as to insure complete and rapid removal of liquid filtered. In the author's laboratory the open end of the filter is somewhat enlarged with a conical reamer (or even the tapered end of a screwdriver) to fit a suitable india-rubber cork, and is hardened by painting round the edge with shellac varnish. Before use, the filters should be thoroughly cleansed from soluble matter, by boiling for two hours with 10 per cent. hydrochloric acid, and thorough washing, and are then dried before washing. About 300 c.c. should be rejected (and if a dry filter is employed, may be used for non-tannin determination), before the portion is taken or evaporation. After use the filters are cleansed by brushing

* Collegium, 1904, p. 249.

† Ibid., 1904, p. 343, 1905, p. 45.

‡ Ibid., 1905, p. 66.

with a soft tooth-brush, and filtering distilled water till it comes through colourless. If, as rarely happens with very muddy solutions, the filter chokes and filters too slowly, the surface may be cleansed by brushing during filtration. It is best to dry the filters after washing, as if kept wet they become very soft. If the filter appears choked with organic matter it may be washed with very dilute ammonia, then with dilute acid and finally with water till neutral before drying. This should always be done if a candle which has been used for extracts with insolubles is employed for solubilised extracts, as otherwise the latter are liable to dissolve out the difficultly soluble matter in the candles.

As it sometimes occurs that filter-candles and the necessary apparatus cannot be obtained, it is well to give some particulars of the method of filtration through paper with correction which was proposed by the author, and which previous to the adoption of the "candle" was the official method of the I.A.L.T.C., and is again made official in cases of difficulty, and the results agree quite accurately with those obtained with the "candle," when the filtration is repeated to optical clearness. The present official directions will be found on p. 213. Those of 1902 were as follows :—

"The filtration of solutions for analysis can be carried out with any paper which is considered most suitable, and if desired kaolin may be used. The amount of tannin absorbed by the filter-paper must be taken into consideration, and a corresponding correction made, which is ascertained by the similar filtration of a perfectly clear tannin solution.

"In order to estimate the error caused by the filter-paper, 500 c.c. of the tannin solution to be analysed is filtered until perfectly clear, preferably by the method of filtration for which correction is to be made. 50 c.c. of this clear solution is now evaporated to dryness, dried and weighed, to determine "total soluble No. 1." A second portion of the same filtrate is now filtered exactly in the manner for which correction is to be made, and 50 c.c. of this filtrate evaporated, dried and weighed. This residue is No. 2. Subtracting No. 2 from No. 1 gives the correction which is necessary to add to the "total soluble" found in analysis.

"It is advisable not only in the analysis but also in the second estimation for correcting the filter-error, that at least the first 150 c.c. which passes through the filter-paper should be discarded,

or used for detannisation, and the next 50 c.c. used for evaporation. During the whole filtration it is advisable that the filter should be kept as full as possible. Where kaolin is used to get a clear filtrate the same quantity should be weighed in each case. One or two grammes are recommended. This is washed by decantation with about 75 c.c. of the tannin solution, and then washed on to the filter-paper with a further quantity of the tannin solution, of which 200 c.c. are filtered as above."

As filtration by the candle may be assumed to need no correction, an alternative method is to filter solutions to optical clearness by the candle, which is usually possible by repeatedly returning the filtrate; and also by the method for which correction is to be made, when the difference in weight on evaporation of 50 c.c. is the required correction. It must be clearly understood that an average correction only is required, since of course the determination for every sample of material and every sheet of paper is impracticable.

In practice it has been found that on the average of many determinations a correction of about $+0.005$ gm. must be added to the residue from evaporation of 50 c.c. of any tanning material through Schleicher and Schull's "605 extra-hard" of 17 cm. diameter; for S. and S. 590 the correction is negligible; Dreverhoff's 311, 15 cm., requires $+0.002$, and the use of 2 gm. kaolin about $+0.0025$ gm. in addition to that required by the filter-paper. Of course different filters, even out of the same packet, will often yield different corrections, but as the whole correction amounts to under 0.7 per cent. on an oakwood extract, slight fluctuations are not of great practical importance.

Perhaps, for the sake of completeness, some allusion should be made to the earlier methods of extraction, which for ordinary purposes have fallen out of use, since it has been recognised that with many materials heat must be sparingly employed. In early times, and for the weak infusions required by the Löwenthal method, it was customary simply to boil a weighed quantity of the finely powdered material with a liter of water for half an hour or more, and to make up the whole, including the solid matter, to 1 liter. This method gives in many cases very constant results, though somewhat below those obtained by percolation, but from its simplicity may sometimes prove useful where merely comparative results are required. A much more accurate method

was that formerly employed by Prof. von Schroeder, who, however, relinquished it in favour of Koch's method, described above.

Von Schroeder's extraction apparatus consisted of a perfectly cylindrical vessel of cast tin, about 12.5 cm. deep and 7 cm. diameter. A strainer covered with fine muslin fitted it like a piston. The powdered material was placed in the cylinder, and stirred up with 200 c.c. of cold water. At the end of an hour the piston was inserted and pressed down gently, the clear liquor poured off, and the process four times repeated with hot water at intervals of half an hour, placing the cylinder in a water-bath. The liquor was made up to 1 liter, and, if necessary, filtered.

To determine separately the "easily soluble tannin" (viz. that extracted by cold water), Real's press was employed, which consisted of a cylinder, fitted with a tap at the bottom, and a water-tight cover at the top, with a tube through which water was forced by the pressure of a column of liquid. A small sieve, covered with a disc of linen, was placed in the bottom of the cylinder, and on it the tanning material previously thoroughly moistened with water, and the tap closed. The press was then filled with water and left fifteen hours under a pressure of 1½ meter. The tap was then opened and 1 liter allowed to run through in the course of about two hours, and the infusion so obtained was thoroughly mixed by shaking. The material was finally exhausted like a new material in von Schroeder's apparatus to extract the difficultly soluble tannin. Both of these pieces of apparatus are practically superseded by Koch's bottle extractor and its modifications.

An apparatus on the principle of Soxhlet's extractor (p. 285), but made of copper, was introduced by the Vienna Research Institute,* and modifications have been largely used in America, but from the facts already mentioned it will be obvious that continued boiling of tanning extracts is inadmissible. If used at all, it should only be for the last traces of tannin after the bulk has been removed at a lower temperature,† but it has been shown by Eachus‡ that continued steam extraction removes matters which are absorbed by hide-powder, but which do not precipitate gelatin.

* 'Gerber,' 1887, p. 67.

† Journ. A.L.C.A., i. p. 88.

‡ Collegium, 1907, pp. 384, 386.

SECTION XII.

TANNIN DETERMINATION BY THE HIDE-POWDER
GRAVIMETRIC METHOD.

THE official methods of the International Association of Leather Trades Chemists, and of the American Association of Leather Trades Chemists are given in Section XIII., but it is necessary here to explain a few details more fully to give reasons for the exact methods prescribed, and to discuss the various suggested modifications.

An infusion of the tannin material, or a solution of extract, of such a strength as to contain 0.35 to 0.45 gm. of tannin matter per 100 c.c. (or as nearly as possible 0.4 gm.) is prepared by the methods described in the preceding section. The following table gives the approximate quantities required.

Variations from the prescribed dilution are specially apt to lead to errors with materials like quebracho, which contain much "difficultly soluble" tannin.

THE APPROXIMATE AMOUNT OF DIFFERENT MATERIALS TO BE WEIGHED
OUT FOR ANALYSIS TO MAKE UP ONE LITER OF SOLUTION.

<i>Barks, etc.</i>	Grammes.	<i>Extracts.</i>	Grammes.
Algarobilla . . .	8-9	Oak wood, sp. gr. 1.2 or over . . .	15
• Canaigre . . .	15-18	Chestnut (liquid) . .	14
Divi-divi . . .	9	„ (solid) . . .	7 •
Hemlock bark . . .	32-36	Quebracho (solid) . .	6
Mimosa bark . . .	11	„ (liquid) . . .	9-13
Myrobalans . . .	15	Mimosa D . . .	10-12
Oak bark . . .	30-36	Gambier (block) . .	10
Oak wood . . .	50-100	„ (cube) . . .	7
Quebracho wood . .	20-22	Mangrove (liquid) . .	9 •
Sumach . . .	15-16 •	• „ (solid) . . .	7
Pistacia lentiscus . .	20-22	Cutch . . .	7
Pine bark . . .	32	Myrobalans liquid) . .	16
Willow bark . . .	36	Hemlock . . .	10-14
Chestnut wood . . .	45	Pine Bark . . .	16
Mangrove bark . . .	• 10		
Valonia . . .	14-15		
Valonia beard . . .	10-11		
Spent tans . . .	50-100		

Determination of "Total Dry Matter."—It is necessary for the calculation of analyses to determine the amount of moisture present in the sample, since this varies in solid materials to a considerable extent with atmospheric conditions, and in extracts according to the degree to which they have been evaporated. The total weight of substance taken, less the moisture, gives, of course, the "total dry matter." The drying, however, presents difficulties in some cases. On the one hand many tannins are easily alterable by heat, parting with water of combination and yielding anhydrides, and on the other, hygroscopic moisture is obstinately retained. Thus different temperatures and different methods yield varying amounts of moisture, and it is often impossible to define the point where hygroscopic water is driven off, and the loss of chemically combined water begins. A standard method would be to dry at ordinary temperature, and preferably *in vacuo*, over concentrated sulphuric acid, but this is too slow for practical requirements. In dealing with dry materials therefore, it is better in every case, to work with as small a quantity as is permissible, taking into account the accuracy of the balance employed. As it is not possible in the analysis of the tanning materials to obtain an accuracy greater than 0.1 per cent. or one part per thousand, 1 grm. is quite sufficient with a balance weighing to milligrams, and with balances of greater accuracy, proportionately smaller quantities may be employed. In the case of liquid and pasty extracts, 1 grm. should never be exceeded, and if possible it is better to work with smaller quantities. The only exceptions to this rule are such materials as cannot readily be accurately sampled in small quantities, and in this case it may be necessary to weigh out larger quantities even at the expense of additional time and trouble, or to dissolve and dry an aliquot part of the solution as described below. The drying of solid materials is accomplished in basins or other vessels which are preferably fitted with a cover to lessen absorption of moisture during weighing, though with rapid weighing this is not essential. The drying of liquid and pasty extracts is more difficult, and is best done in the flat bottomed shallow basins which are used for the subsequent determinations, and which should be 7 or 8 centimeters in diameter and capable of holding at least 50 c.c. In such basins the extract spreads itself to a thin layer; while, if the basins are

rounded, it collects at the bottom and dries on its surface, forming a coherent coating from which the moisture of the interior of the mass escapes with great difficulty. In cases where extracts are solid or too thick and pasty to spread themselves without assistance, the addition of 20 or 25 c.c. of water, in which the extract is dissolved on the water-bath in the basin, will considerably facilitate drying. The author proposed the use of alcohol for the same purpose, which certainly leads to rapid drying, but on the whole he is of opinion that water is to be preferred. Where extracts will dissolve in water to a turbid solution which can be thoroughly mixed by shaking, the best method of determination of both water and dry matter is to mix the liquid thoroughly, after making up to the liter (or 2 liters where it is desirable to weigh a larger sample), and before filtration, and to pipette 50 c.c. into a basin as usual. The residue obtained in this way $\times 20$, or the sum of duplicate determinations $\times 10$, is obviously the dry matter contained in the substance weighed out for analysis, and the difference between this and the original weight is the moisture; while the difference between the "dry matter" and the "total soluble" obtained by evaporation after filtration is the matter "insoluble at $15^{\circ}\text{C}.$ "

As regards drying apparatus, the German Section of the I. A. L. T. C., have selected the Moeslinger drying oven, which is simply a water jacketed oven with small compartments, the interior of which cannot reach a temperature exceeding 95° – $98^{\circ}\text{C}.$ In this apparatus drying is, in the author's opinion, much too slow, at least 8 or 9 hours being required with many materials to obtain approximately constant weight. This length of time is objectionable not only on account of the delay, but because in most tanning materials oxidation, leading to a gain of weight, goes on at the same time as drying; so that in some cases the sample begins to gain weight instead of remaining constant, and even the lowest weight found must be too high, as oxidation no doubt occurs more or less during the entire drying. The American Leather Chemists' Association have officially adopted Reed's Combined Evaporator and Dryer,* which seems open to the same objections. In the writer's opinion a preferable method is the use of an air-oven heated to a temperature of 100° – $105^{\circ}\text{C}.$, in which the drying is much more rapid, while

* Journ. A. L. C. A., 1906, p. 32; see also Collegium, 1907, p. 140.

the danger of oxidation is probably not increased. Great care, however, is required even in ovens with automatic regulation of temperature that 105°C. is not exceeded in any part of the oven; and that the vessels, especially if of metal, do not come in contact with the heated walls. There can be little doubt that the vacuum drying oven is the most perfect means for drying tannin residues, accomplishing the work in two or three hours with as little exposure to oxidation as possible. There seems no reason why the vacuum-oven should be used at a temperature below 100°C. , as from its expense it cannot become the ordinary means of drying in small laboratories, which must dry at about 100°C. , and greater differences are likely to arise between this and working at a temperature at 60° or 70°C. than would occur by drying at 100°C. for the shorter period required by *in vacuo*. After drying for a sufficient length of time, the sample is cooled in a desiccator, and rapidly weighed; and is then returned to the oven for half an hour or more, and the process repeated, placing the weight previously found upon the scale, so that the weighing can be almost instantaneous. If the loss of weight exceeds 2 milligrams, the sample should again be returned to the oven and the process repeated. If larger quantities than 1 gm. are being dried, a somewhat larger margin may be allowed.

Determination of "Total Soluble" Matter.—50 c.c. of the solution filtered by one of the methods described in the previous section, is measured with a pipette into a weighed glass or porcelain basin as described in the previous paragraph, and evaporated to dryness on a water-bath.* It is then dried eight hours, or overnight, in a water-oven at 100°C. , or, preferably, three hours in an air-oven heated to 100° – 105°C. , or two hours in a vacuum-oven at 100°C. , cooled in the desiccator† and weighed till constant as before. About three hours in the vacuum-oven

* Platinum, nickel, or aluminium basins may be substituted for porcelain with some gain in rapidity of evaporation. Platinum is important where the ash of the residue must be determined, as in the analysis of old liquors, and but for its cost is most advantageous; nickel is less fragile than porcelain, but not suitable for ignitions, and aluminium is not to be recommended unless lightness is of great moment, as it is often attacked by the liquors to a slight extent; and this is specially apt to occur with the impure commercial aluminium used for cooking utensils. If it is used, care must be taken to prevent contact with the copper water-bath; which sets up galvanic action and increases oxidation.

† It is important that dry calcium chloride, or some other good water-absorbent, should be employed in the desiccator, as the dry residues are very hygroscopic.

and five hours in the air-oven are generally sufficient. Ultimately the residue may begin to gain weight from oxidation, and absolute constancy cannot always be obtained. In case of gain being noticed, the minimum observed weight must be taken, and this itself will obviously tend to be in excess of the truth, either from oxidation or imperfect drying, or both. The weight obtained after deducting that of the basin is that of the soluble matter of $\frac{1}{20}$ part of the substance originally weighed out, and hence the percentage is readily obtained by dividing double the weight of the residue in milligrams, or the sum of two duplicate determinations, by the weight in grams of substance employed.

Determination of "Soluble Non-Tanning Matter."—Up to June 1907, the official I. A. L. T. C. method of detannisation has been by the hide-powder filter (see p. 211). The syphon-filter generally employed (Fig. 14) is of a bell-shape, of a total length of 7 cm. with a diameter of 3 cm. in the cylindrical part, and 1.8 cm. in the neck, and resembles a bottle from which the bottom has been removed. Into the neck of this is fitted an indiarubber cork, with a piece of fine glass tubing about 30 cm. long projecting slightly through the cork, and bent into the form of a syphon. The short limb of this within the bottle is plugged with a tuft of cotton or glass wool, and the bottle is uniformly filled with between 6.5 and 7.5 gm. of hide-powder. The satisfactory filling demands some practice, and depends much on the quality of the powders. If

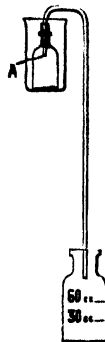


FIG. 14.

the powder is too tight, or swells too much on being wet, the filter refuses to run, or runs too slowly; if too loose, the liquid forms channels and is not properly detannised. With pure hide-powders there is a tendency for the liquid to pass up the sides of the glass, and it is best to pack up pretty firmly round the sides, leaving it as loose as possible in the centre; but this difficulty has been almost entirely overcome by the admixture of cellulose (not exceeding 20 per cent.) with the hide-powder, so that it can usually be packed firmly and evenly. The use of cellulose for this purpose was first proposed by F. Cerych.* When full, the powder is kept in place by a piece

* 'Gerber,' 1895, p. 241; cp. also *ibid.*, 1896, p. 62.

of muslin secured over the bottom of the bottle with an india-rubber band. If the powder does not entirely fill the bell, the vacant space may be occupied with purified cotton or glass wool. The packed filter is placed in a beaker or tumbler, with its open bottom resting on the bottom of the glass, and the tanning infusion is added very gradually little by little, so as to wet the powder by capillary absorption. When the filter and tumbler are filled with liquid, the syphon is started by sucking with a piece of india-rubber tube, and the filtered liquid is allowed to drop into a gauged cylinder. The first 30 c.c. are placed on one side, and the next 60 collected, from which 50 c.c. are pipetted, and evaporated for non-tannins. This should be quite or nearly colourless, and if a little of the liquid is now allowed to drop from the syphon into the first 30 c.c., no cloudiness should be produced. The soluble matter of the hide-powder contained in the first 30 c.c. is in this way a much more delicate test for tannin than any gelatin solution. Should the filtrate not be perfectly free from tannin, the entire operation must be repeated, using a more diluted solution.

The time required to obtain the necessary quantity of filtrate with a well-filled filter does not exceed 1 hour after the hide-powder has been thoroughly wetted; but a somewhat longer time is not injurious. As it is extremely difficult to regulate the rate of filtration by the tightness of packing, it is usually best to use a piece of rubber pipe and a pinchcock on the syphon to regulate the flow to a rate of one drop in two seconds, which will give about 90 c.c. per hour. Very slow filtration, extending over more than two hours, usually increases the hide-substance dissolved, and consequently the amount of non-tannins found. Corych shows that high temperature of the laboratory during filtration also increases the amount of dissolved hide-substance, and advises that the temperature should be kept below 20° C., even if in hot weather artificial cooling has to be resorted to. The temperature also influences the amount of "insoluble reds" (cf. p. 181).

The most serious objection to the filter is that it undoubtedly absorbs other substances, such as colouring matters and acids in addition to the actual tannic acid present. This defect is necessarily common to some extent to all hide-powder processes, but is specially marked with the filter, in which the completely

detannised liquor passes through a layer of completely untanned powder. As the absorptive power of raw hide for non-tannins is much greater than that of leather, the composition of the filtrate is never constant, the absorption of non-tannins constantly decreasing from the beginning to the end of the operation. In some cases the absorption of non-tannins is not of very serious importance from a practical point of view, but with materials such as sumach, which contain a large proportion of gallic acid, the latter is almost entirely absorbed by the hide, and not being volatile, is of course reckoned as tanning matter. A similar error occurs with sour liquors containing lactic acid. Several methods of overcoming this have been suggested (see p. 242), but none have hitherto proved entirely successful. Weiss found that the addition of common salt to the liquor * greatly reduced, but did not overcome it, while the presence of salt interfered with the drying of the residues. The writer found that alcohol added to the liquor prevented the absorption of gallic acid, but, if used in any large quantity, also interfered with that of tannin. Meerkatz† employed barium carbonate to neutralise the acids present in sour liquors. Barium salts remain dissolved in the liquors, and are taken up at first by the hide filter, but after passing 300 c.c. are said to be no longer absorbed. Apart from the difficulty of securing complete absorption of tannin after passing so much as 300 c.c. through an ordinary hide filter, the gallic acid salts rapidly become partially insoluble by oxidation, and apparently tannin is also liable in some cases to be precipitated, so that few chemists have succeeded in carrying out the process satisfactorily. In addition, it has been observed by the writer that neutral salts of weak acids, such as borax and sulphites, paralyse the absorption of tanning matter by hide, which precludes the use of such salts for neutralising acids in liquors, and is not without bearing on Meerkatz's process. It has, however, been found that the use of chromed hide-powder (p. 204) considerably diminishes, though it does not prevent, the absorption of acids, and it entirely overcomes the swelling which with ordinary hide-powder is very troublesome in presence of acids, frequently causing the filter to choke and refuse to run. Some particulars as to the absorption of substances other than tannin by hide-powders are given on

* Gerler, 1887, p. 139.

† Op. cit., 1889, p. 73.

pp. 208-210, but it may be remarked that most natural colouring matters and many artificial ones are completely removed. Thus the total tannin and colouring matter of a logwood extract may be estimated readily in the same way as tanning matters.*

A dry lightly chromed hide-powder has been prepared by Dr. Paessler,† which obviates many of the difficulties incident to the use of ordinary hide-powder in the filter-bell, being easier to prepare and to free from soluble hide-substance, and not so liable to swell and choke the filter in the presence of acids, so that its results show distinctly better concordance. It has, however, the defect of absorbing in most cases somewhat more non-tannins than even the unchromed powders, and therefore gives results 1 to 2 per cent. higher in "tanning matters." On this account it has never been accepted as official by the International Association, though it was for a period adopted by the German section. Used for the shake method (p. 202), while fresh, it gives results in fair accordance with wet chromed powders.

Preparation of Hide-Powder.—The method adopted by the Research Institute at Vienna is as follows: A fresh ox-hide is well soaked and washed to free it from blood and dirt, and is limed for eight days, fleshed and unhaired as usual, and cut up into pieces of about 1 cm. sq. It is then treated with dilute hydrochloric acid, containing say 1 per cent. of pure concentrated acid, until slightly swollen, and is washed with many changes of clean cold water till the acid is again completely removed. The pieces are next spread upon linen, and dried as rapidly as possible in a current of cold air. Immediately before grinding it is dried for a considerable time above steam pipes at a temperature of about 40° C., and at once ground repeatedly through a "Favorita" mill (constructed by H. R. Gläser, of Vienna), which is on the same principle as the Schmeijer mill and the "Devil" disintegrator; that is, consisting of a fixed and a rotating disc with alternated rings of teeth. The powder is first ground with these discs somewhat apart, but finally with them close set. The method is almost identical with that described by Von Schroeder in the 'Bericht der Commission zur Feststellung einer einheitlichen Methode der Gerbstoffbestimmung,'‡

* Compare Kopecky, Journ. Am. Lea. Ch. ii., p. 24.

† Collegium, 1906, pp. 27, 412.

‡ Cassel, 1885.

who, however, dried at a higher temperature, and employed a specially made steel mill of the "bell" or "coffee-mill" pattern.

Little advantage is to be gained by re-washing a good powder without the addition of paper, as treatment with alcohol in the way recommended by Cerych renders it repellent of water and unsuitable for the filter; while, if dried in warm air a further portion of the hide-substance becomes soluble during the drying. Bad powders are, however, much improved by washing, drying as rapidly as possible at a low temperature, and re-grinding.

Good powder for the filter method should be white, soft and woolly, and when well shaken into a liter flask by beating on the hand, should not weigh much over 200 grm. If 6-8 grm. are treated in the filter with distilled water, the first 50 c.c., after rejecting 30 c.c. as in analysis, should not yield more than about 4 mgr. of dry residue, and a similar limit should be reached after shaking with water, as for analysis. For the filter method, the powder must be absorbent and readily wet by water, but for shaking this is of much less consequence, and a denser and less woolly powder will answer quite well.

It has been stated that the age and sex of the animal, and the portion of the hide taken, have considerable effect on the quality of the powder, but the subject requires further investigation. It has been shown by Kopecky that the absorption of the grain differs from that of the more fibrous tissue, and good powders can be made from flesh splits. The absence of grease is very important, especially for the filter method.

It is important that hide-powders should not be made from hide which has undergone any sensible degree of putrefaction. If not carefully washed, such powders contain a large amount of soluble organic matter, and hence cause the non-tannins to appear too high. If this defect is overcome by careful washing, it becomes obvious that the changes which have taken place in the fibre have given it an abnormal power of absorbing some of the colouring and other matters which are present in tanning materials, and that hence the non-tannins come out too low and the tannins, of course, proportionately too high. Even if such powders still contain a sensible amount of soluble matters, the results in non-tannins are sometimes low, since the dissolved hide-substance is precipitated by tannins and colouring matters.

Hence the futility of attempted corrections for soluble matter! This was first pointed out by Koch,* and has since been confirmed by Fiebing, Cerych and others. Such powders may generally be recognised by their putrid smell and greyish appearance.

As regards the preparation of chromed hide-powders, see also pp. 203, 205, 215, 218. Various substitutes for hide-powder have been from time to time proposed. Simand and Weiss very early employed powdered "osseine," the gelatinous tissue of bones which have been freed from calcium salts by treatment with dilute hydrochloric acid, but subsequently abandoned it in favour of ordinary hide-powder. Gelatin or gelatinised paper rendered insoluble with formaldehyde has been tried, but seems impossible to prepare of uniform quality. Ordinary hide-powder similarly treated is very insoluble, but appears to become less absorbent on keeping and is different in its results from untreated powder. Recently, Wislicenus† has proposed the use of the porous alumina produced when aluminum is wetted with a mercuric chloride solution, but its absorptive power is not the same as that of ordinary hide-powder and seems to vary in different specimens. Liquors have been detannised by egg or blood albumen which is precipitated on heating, but it would be difficult to obtain a sufficiently pure product to have no residue, and other things beside tannins would be carried down by its precipitation. The present writer obtained fairly good results in some experiments in which a very pure gelatine was used as a precipitant and afterwards itself precipitated by strong alcohol and a little formaldehyde, but the method was expensive and did not seem worth pursuing.

Calculation and Statement of Analyses.—It is usual in hide-powder analyses to state the constituents under the following headings: "Tanning matter absorbed by Hide," "Soluble non-tanning Matter," "Insoluble at 15° C.," "Moisture." To obtain these, in addition to the determination of tanning matter just described, a moisture determination is necessary. This must be carried out at the same temperature as is used for drying the evaporated residues, but in the ordinary water-oven, gambier and some other extracts take an inordinate time to dry. At most,

* Ding. Polyt. Journ., 1891, cxlxxx. pp. 141, 159.

† See footnote, p. 175.

1 to 2 grm. need be employed, if a balance of ordinary delicacy be available, and in the case of liquid extracts and gambier, 1 grm. should not be exceeded.

The calculation is made as follows: The percentage of tanning matter is obtained by subtracting that of Soluble Non-tannins from that of Total Soluble. The Insoluble is similarly got by deducting the Total Soluble from the Total Dry Matter obtained in the moisture determination. The four must necessarily add up to exactly 100 if the calculation is correct. If an extract is quite free from insoluble matter, it occasionally happens that the Total Soluble apparently exceeds the Total Dry Matter, in consequence of oxidation during drying. In this case, in which the difference should not at most exceed a few tenths per cent., it is best to neglect the Total Soluble, and use the Total Dry Matter in the calculation of the Tanning Matter.

It is often desirable to determine ash and inorganic matter in the residue of the moisture determination, but it should not be added in with the other constituents, as it is impossible to say whether it is derived from the soluble or insoluble portion, unless the residues of Total Soluble are also ignited. The ignition should be very gentle till all the carbon is destroyed, on account of the possible presence of fusible salts, and if necessary the methods given for such cases on p. 11 must be adopted. In sumachs, ash is important as affording an index of the degree of "ventilation" or removal of sand, which is often ferruginous, and darkens the colour of the liquor and leather. The total ash should not much exceed 6 per cent. in a really pure sumach. The natural ash of the sumach may be practically removed from the siliceous sand, mostly of volcanic origin, by washing with dilute hydrochloric acid and again igniting. If limestone is present, it will of course go with the ash. Dr. Turnbull determines sand and the heavier mechanical impurities by shaking a weighed quantity with commercial carbon tetrachloride in a pear-shaped separating funnel, with a wide-bore stopcock, when the sand settles to the bottom and can be decanted into a basin, dried, and gently ignited. Sumachs frequently contain among the sand particles of magnetic oxide of iron, which may be detected by sorting the dry sumach with a magnet, to the edge of which the dark metallic looking particles adhere, and are easily seen with a lens. They may be

distinguished from actual metallic iron by solution in a drop of dilute sulphuric acid, if necessary, on a glass slip under the microscope. The magnetic oxide dissolves without effervescence to a yellow solution, the metallic iron to a colourless one with evolution of hydrogen. The total iron in the ash may be determined colorimetrically (p. 40). Barks and bark extracts usually contain a little manganese, which colours the ash green if fused. In extracts the quantity and character of the ash often give useful hints as to the methods of manufacture.

Artificially solubilised extracts usually contain an increased quantity of soluble alkaline carbonates.

As has been mentioned on p. 173, the earliest form of the hide-powder gravimetric method consists in macerating a certain quantity of powder with the liquor to be detannised. The principal disadvantage of this method was the length of time which it required, which was not merely inconvenient, but led to the solution of portions of the powder, especially in warm weather, when putrefactive changes are liable to occur, but which was not entirely prevented even by the use of antiseptics.

A much quicker process, which lessened the difficulty just named, was introduced by an American chemist, Dr. Yocum,* who employed a "shaking machine" originally introduced for the mixing of summer drinks shown in Fig. 15, but any satisfactory mode of vigorous agitation can be used, and bottles fixed in a



FIG. 15.

frame, rotated not less than 60 revs. per min., answer very well. It was found that by shaking the tanning liquor in this way with the wet powder, the time required for detannisation could be reduced to about ten minutes. In order to obtain a powder as free as possible from soluble matter, it was previously shaken with water and used in the wet state, an allowance being made for the water so introduced. In this way it was possible to obtain very good results, though usually 1 or 2 per cent. lower in tannins than those given by the filter method, and as the

* *Leather Manufacturer*, 1894, No. 9.

powder was washed immediately before use, inferior powders could be used which were unsuitable for the filter. In 1901,* at the suggestion of Director Eitner, the Vienna Research Institute experimented with chromed hide-powder, and finding that it reduced solubility and swelling without materially influencing the absorption of tannins, adopted as their general method, a dry chromed powder, and maceration. In the autumn of the same year, light chroming of a wet powder with chrome alum was adopted by the American Leather Chemists (Association of Official Agricultural Chemists), and has remained their official method up to the present date, and their directions are given in Section XIII., together with those of the International Commission as adopted by the International Association. In practice the quantity of powder required for the analyses to be made is stirred in a large beaker with 25 times its weight of distilled water, and allowed to soak for 24 hours, 1.5 per cent. of chrome-alum previously dissolved in water being added at the beginning of the operation, and 1.5 per cent. more, not less than eight hours before its end. The powder is freed from the liquor by squeezing through linen, and the washing is continued till the wash-water no longer gives a precipitate with barium chlorid†; and is then well squeezed out in linen, preferably with aid of a press. The damp squeezed powder is now roughly weighed, to determine approximately what quantity it is necessary to take, to give 12–13 grm. of the original air-dry powder to each estimation (air-dried powder contains about 15 per cent. of moisture), and a portion is accurately weighed in a basin, and dried, first on the water-bath, and then in the drying oven, to determine its moisture by loss. The approximate amount of powder required for each determination (if possible a round number of grams) is now weighed into as many bottles of about 600 c.c. capacity as determinations are to be made, 200 c.c. of the filtered liquors, prepared as before described, are introduced into each bottle, and the bottles are then each shaken in the machine for ten minutes. The contents of the bottles are now filtered through S. and S. 590 paper with the addition of 2 grm. kaolin and the liquor is returned to the funnel till a clear filtrate is obtained,

* 'Gerber,' 1901, ii, p. 1.

† Strictly speaking, small traces of sulphates continue to be removed almost indefinitely.

of which 50 or 100 c.c. are evaporated as in the international method. It is now necessary to accurately correct the residue obtained, for the amount of water carried in by the wet powder. The loss of weight of the powder which has been dried, divided by its wet weight, gives the water contained* in each gram of wet powder, and this multiplied by the weight of wet powder added to the liquor, gives the weight in grams (or volume in c.c.) of water which has been added to each 100 c.c. of liquor. Consequently, if the residues found be multiplied by this weight plus 100, and the product divided by 100, the weight will be obtained which should have been given by 50 c.c. of undiluted but detannised liquor; and from this, the non-tannins are calculated exactly as in the case of the residues from the filter process. Of course, in practice, a factor is found, by which it is simply necessary to multiply all the residues, to correct them to undiluted weight. The process sounds somewhat complicated, but in reality, where a large number of determinations have to be made, is quite as quick, if not quicker than the filter method.

A rather considerable disadvantage in the use of wet chromed hide-powder is that it will not keep for any length of time in a moist condition, and consequently has to be prepared from a good hide-powder as required, and that it is very difficult if not impossible to free the wet hide-powder completely from soluble salts and especially from sulphates before it has undergone some decomposition. To overcome this difficulty various attempts have been made to prepare a dry chromed hide-powder, but with very varying success, owing to the conditions not being fully understood. In 1901*, the Vienna Research Station adopted a method of preparing such a powder, which, while it gave somewhat higher results in non-tannins than the filter method, was otherwise satisfactory, and was much less affected by the presence of acids. The exact method of preparation and use of this powder was not published until 1905.† Prior to this time, work had been going on, on the same subject, in the laboratory of the Leeds University, and Mr. F. Kopecky‡ had devised a mode of making and using chromed powder which was not only cheap

* 'Gerber,' 1901 (No. 634), p. 29. Ibid., 1902 (No. 663), p. 104.

† Ibid., 1905 (No. 745), p. 260; (No. 746), p. 275.

‡ Collegium, 1904, p. 211.

but apparently considerably more accurate in its results than the filter-method with ordinary hide-powder. When the Vienna Institute finally published the details of its method, it proved to be almost identical with that which had been also developed at Leeds, but Mr. Kopecky's mode of preparing the powder appeared to have considerable advantages in cheapness and ease of manipulation over the chroming of a ready prepared hide-powder, which was adopted at Vienna. Raw pelt is extremely difficult to grind, and air-dry hide, however carefully washed and purified, cannot be ground satisfactorily even with the small amount of moisture which it contains, without a partial gelatinisation by the heat developed by friction, which leads again to an increase of soluble matter. The preparation of Kopecky's powder is as follows:—

The belly-portions of sound lined hides are delimited either by means of a sour bran drench or by organic acids (preferably acetic or formic), and after thorough washing are lightly and evenly tanned with a basic chrome liquor containing 10 per cent. of chrome-alum on the weight of wet pelt, and 3·5 per cent. of crystallised sodium carbonate, which is dissolved separately and gradually added to the chrome liquor. This liquor is added in small quantities to the pelt placed in twice its weight of water in a revolving drum, so that the tannage is complete in about 18 hours. It is important that the tannage should be a slow one in a suitable volume of liquor in order that the penetration may be as uniform as possible throughout the pelt. The chrome leather, after lying for twelve hours wet with the liquor, is neutralised with 3 per cent. of borax for one hour, washed in three changes of water, set out thoroughly and split, as it is found that the grain part is unsuitable for hide-powder and is better made use of for other purposes. Instead of splitting at this stage, it would, in many cases, be more convenient to split from the limes, chroming only the flesh. The chromed splits are now dried slowly, cut up into pieces, and ground in a suitable mill, a toothed-disc mill ("Favorita," made by Glaesser and Co., of Vienna) being employed at Leeds. This ground powder is again thoroughly washed, dried and re-ground, and is then ready for use. In place of splitting, a satisfactory powder may also be made by shaving the material thin on an ordinary shaving machine, and subsequently drying, washing and

grinding the shavings. It is important, however, that the chroming should be done according to the directions given, and as this chroming is somewhat light it may be desirable to return the grains to chrome liquor after splitting or shaving, before finishing them for leather purposes.

The great difficulty in the use of chromed hide-powder is that when thoroughly dried it absorbs water extremely slowly. It is, therefore, necessary to weigh out the quantity of the air-dry powder which is required for the estimations expected, and mix it with water to a thin paste, and allowing it to soak for at least six hours (preferably overnight); 10 gm. of powder being allowed for each determination. After soaking, it is freed as completely as possible from water by squeezing in cheese-cloth, mixed with a fresh quantity of distilled water, and again squeezed out as tightly as possible and well mixed. The total weight should be about 30 gm. of wet for each 10 gm. of air-dried powder, containing about 70 per cent. of moisture, in the wet, and 10 per cent. in the air-dry state. With practice it is easy to get within 1 per cent. of the moisture stated in the wet powder. If too wet, mixing on filter paper will rapidly reduce moisture. Accurate determination of moisture is unnecessary.

50 gm. of the wet powder is used for the detannisation of 150 c.c. of the tannin solution, which may be conducted in a wide-mouthed bottle, cylinder, or beaker (tumbler). Either shaking or maceration will give approximately equal results, but further experience is needed to determine the time of shaking exactly equivalent to one hour's maceration, which Kopecky regarded as the standard method. Longer maceration, or repeated filtering will slightly increase absorption. The mixture is now poured on a filter-paper in a funnel covered by a clock-glass and is allowed to run through, and *twice* returned to the funnel.

50 c.c. of the solution is evaporated as usual and corrected by multiplication by $\frac{150 + \text{water of 30 gm.}}{150}$, the moisture being determined on a portion of wet powder.

Some few dark coloured materials, and especially some quebrachos and mangroves, of which the infusions cannot be detannised by the hide-filter without dilution, also require the use of 40 instead of 30 gm. of wet powder in the present method.

The method is equally adopted for the estimation of tannin in fresh materials and in sour liquors, being little affected by the presence of organic acids, and answers excellently while the powder is fresh, but it has unfortunately been found that its absorbency lessens on keeping. This appears to be a defect common to all chromed powders, though less obvious when the chroming is light, and is probably due to a gradual loss of moisture which the fibre will not re-absorb. It is to be hoped that Kopecky will succeed in so modifying his powder as to overcome this difficulty, since the use of a dry chromed powder is very convenient.

It may be taken as proved, that either chromed or unchromed hide-powder in moderate excess will absorb the whole of the actual tannins contained in any solution of the prescribed strength; but it has already been pointed out (p. 196) that the so-called "tanning matters" absorbed contain many other things which are not truly tannins, or perhaps strictly even "tanning matters." It therefore becomes of importance to know what is actually absorbed under given conditions, and, though it would be difficult to make any really exhaustive investigation, the following will throw some light on the subject.

One of the earliest attempts to test the matter was that of H. R. Procter, in 1887,* who pointed out that while dextrin was unaffected, glucose was not only passed through but dissolved a portion of the hide-powder, so that the dry residue was increased by filtration. It is possible that this may have been due to the presence of traces of lime in the somewhat primitive hide-powder then in use, as experiments by Prof. Weiss and by Procter and Blockey quoted below show an increase of residue with dextrin and chromed powder, but none with plain powder, while glucose was indifferent with both.

Ordinary tanning matters contain many substances, such as gallic acid, catechins, etc., which belong to the class of astringent substances, though not actually tannins. The absorption of several of these and analogous compounds, as determined by Procter and Blockey,† is given in the following tables.

* Journ. Soc. Ch. Ind., 1887, p. 94.

† Op. cit., 1903, p. 482; Collegium, 1903, pp. 114, 124.

EFFECT OF THE ADDITION OF VARIOUS NON-TANNINS TO QUEBRACHO.

Material employed.	Grms. per Air-dry.	Grms. Soluble per 100 c.c.	Percentage on Dry Quebracho Tannin taken.						Percentages of Dry Non-Tanning Substance estimated as Tannin.			
			Filter Method		Shake Method.		Washed Powder.	Non-Tannins.	Filter Method.	Chromed Powder.	Washed Powder.	Filter Method.
			Tannins.	Non-Tannins.	Plain Powder.	Chromed Powder.						
1. Quebracho tannin	5.0	0.442	96.1	3.9	93.9	6.1	92.0	8.0
2. Quebracho tannin	5.0	0.837	173.1	16.3	138.2	51.2	135.2	54.2	89.4	49.6	48.3	..
3. Quebracho tannin	5.0	0.843	190.8	89.8	88.3	102.5	88.3	102.5	5.4	-6.2	-4.1	..
4. Dextrin	5.0	0.651	147.2	94.2	53.0	90.6	56.6	90.1	57.1	-4.0	-4.0	..
5. Glucose	5.0	0.470	106.3	97.5	8.8
6. Glac. acetic acid	5.0	0.556	125.9	121.3	4.6	112.8	13.1	115.0	10.9	97.3	73.0	88.8
7. Quinol	5.0	0.584	132.2	125.1	7.1	128.2	14.0	120.0	12.2	90.1	106.5	87.0
8. Catechol	5.0	0.440	100.0	94.9	5.1	88.6	11.4	89.1	10.9
9. Quebracho tannin	5.0	0.536	126.4	117.8	8.6	110.9	15.5	108.2	18.2	86.7	84.5	72.3
10. Quebracho tannin	5.0	0.668	151.8	144.3	7.5	115.2	36.6	118.4	33.4	95.4	51.5	56.6
11. Gallic acid	5.0	0.540	122.7	115.3	7.4	98.8	23.9	100.7	22.0	89.9	44.9	51.1
12. Quebracho tannin	5.0	0.646	146.8	139.8	7.0	117.0	29.8	122.4	24.4	95.9	60.7	71.2

The following table by Prof.¹ Weiss*, referring to the dry chromed powder in use at the Vienna K.K. Institute for Leather Industry may also be quoted.

	Dry Residue per 100 c.c.		
	Original Solution.	Chrome Powder Filtrate.	Plain Powder Filtrate.
Tannin	0'418	0'015	0'011
Tannin + Cane-Sugar	0'418 2'806 }	2'770	2'768
Tannin + Glucose	0'418 1'035 }	1'043	1'037
Tannin + Gallic Acid	0'418 0'405 }	0'385	0'367
Tannin + Dextrin	0'418 0'778 }	0'817	0'772
Extractum Graminis	0'623	0'618	0'599

Further tables will be found in Collegium, 1906, pp. 421, 432, 442, 443; and 1907, pp. 50-56, and 165.

It may further be stated that all acids and strong bases are absorbed by hide (though the latter can hardly be present in a tanning liquor); and that many metallic salts and most dyes are also absorbed.

SECTION XIII.

THE OFFICIAL METHODS OF TANNIN ESTIMATION.

IN the preceding Sections the development of the hide-powder method of tannin estimation, and the principles on which it is based, have been discussed at some length, and all that seems further necessary is to give the full text of the present official methods of the International Association and the American Associations of Leather Trades Chemists, together with a few notes on their differences and on special points in their manipulations. These notes are referred to by means of

¹Gerber, 1905 (No. 746), p. 277.

numbers in the text. The divergences between the two methods are small and unimportant, and the International Association accepts the analyses of members of the American Association as official when done by the American method.

The following* is the text of the method recommended by the International Association, and described in their organ "Collegium," 1907, p. 249.

THE NEW "INTERNATIONAL" METHOD OF TANNING ANALYSIS.

By resolution of September 19, 1906, the I. A. L. T. C. in conference at Frankfort a. M., appointed an International Commission to investigate the various methods of tanning analysis and test by means of comparative work, and finally to report their conclusions to the Executive Committee on or before April 1, 1907.

The Executive Committee was empowered, if necessary after further reference to the Commission, to adopt their report and to make the same the official and compulsory method of the I. A. L. T. C. The Conference specially stated that the retention of the filter bell was not a *sine quâ non*.

The Analysis Commission consisted of the following: For Scandinavia, V. Bocgh; Italy, Baldracco; France, Meunier; Belgium, Wauters; Germany, Paessler; America, Reed; Austro-Hungary, Eitner; England, J. G. Parker, as representing the extract trade, Lepetit; with Procter as chairman; Berger as collaborator in place of Klenk.

The following are now the final recommendations of the Commission:—

General Regulations.

The Executive Committee have decided that any method which conforms to the conditions of Sections 1 to 4 of the following statement may be regarded as conforming to the recommendations of the International Commission on Tannin Analysis, but that members of the International Association must work according to the detailed directions contained in Sections 5 to 8.

1. *The Solution for Analysis.*—This must contain between 3.5 and 4.5 grm. of tanning matter per liter, and solid materials

must be extracted, so that the greater part of the tannin is removed at a temperature not exceeding 50° C.

2. *Total Solubles*.—These must be determined by the evaporation of a measured quantity of the solution previously filtered, till optically clear both by reflected and transmitted light; that is, a bright object such as an electric light filament must be distinctly visible through at least 5 cm. thickness, and a layer of 1 cm. deep in a beaker placed in a good light on black glass or black glazed paper must appear dark and free from opalescence when viewed from above. Any necessary mode of filtration may be employed, but if such filtration causes any appreciable loss when applied to a clear solution, a correction must be determined and applied as described in Section 6. Filtration must take place at a temperature between 15° C. and 20° C., or the actual temperature shall be stated on the Report.

3. *Total Solids*.—These must be determined by drying a weighed portion of the material, or a measured portion of its uniform turbid solution at a temperature not exceeding 100° C. *in vacuo* or 105° C. in air till constant. "Moisture" is the difference between 100 and the percentage of total solids, and "Insoluble" the difference between "Total Solids" and "Total Solubles."

4. *Non-Tannins*.—The solution must be detannised by shaking with chromed hide-powder till no turbidity or opalescence can be produced in the clear solution by salted gelatin. The chromed powder must be added in one quantity equal to 6 to 6.5 gm. of dry hide per 100 c.c. of the tanning solution, and must contain not less than 0.5 and not more than 2 per cent. of chromium reckoned on the dry weight, and must be so washed that in a blank experiment with distilled water, not more than 5 mgr. of solid residue shall be left on evaporation of 100 c.c. All water contained in the powder should be determined and allowed for as water of dilution.

I.A.L.T.C. Official Method.

The following sections give the detailed method of carrying out the analysis adopted by the I.A.L.T.C. for the use of its own members.

5. *Preparation of Infusion*.—Such a quantity of material shall be employed as will give a solution containing as nearly as

possible 4 grm. of tanning matter per liter, and not less than 3.5 nor more than 4.5 grm. Liquid extracts shall be weighed in a basin or beaker and washed with boiling distilled water into a liter flask, filled up to the mark with boiling water, and well mixed, and rapidly cooled to a temperature between 15° and 20° C., after which it shall be accurately made up to the mark, again well mixed, and filtration at once proceeded with; sumach and myrobalans extracts should be dissolved at a lower temperature.

Solid extracts shall be dissolved by stirring in a beaker with successive quantities of boiling water, the dissolved portions being poured into a liter flask, and the undissolved being allowed to settle and treated with further portions of boiling water. After the whole of the soluble matter is dissolved the solution is treated similarly to that of a liquid extract.

Solid tanning materials previously ground till they will pass through a sieve of 5 wires per centimeter, are extracted in Koch's or Procter's extractor with 500 c.c. of water at a temperature not exceeding 50° C. (2), and the extraction continued with boiling water till the filtrate amounts to 1 liter. It is desirable to allow the material to soak for some hours before commencing the percolation which should occupy not less than 3 hours, so as to extract the maximum of tannin. Any remaining solubles in the material must be neglected, or reported separately as "difficultly soluble" substances. The volume of liquid in the flask must after cooling be accurately made up to 1 liter.

6. *Filtration.*—The infusion shall be filtered till optically clear (3) (see Sect. 2). No correction for absorption is needed for the Berkefeld candle, or for S. and S. 590 paper if a sufficient quantity (250–300 c.c.) is rejected before measuring the quantity for evaporation; and the solution may be passed through repeatedly to obtain a clear filtrate. If other methods of filtration are employed, the average correction necessary must be determined in the following manner. About 500 c.c. of the same or a similar tanning solution is filtered perfectly clear, and after thorough mixing 50 c.c. is evaporated to determine "total soluble No. 1." A further portion is now filtered in the exact method for which the correction is required (time of contact and volume rejected being kept as constant as possible) and 50 c.c. is evapo-

rated to determine "total soluble N^o. 2." The difference between No. 1 and No. 2 is the correction sought, which must be added to the weight of the total solubles found in analysis. An alternative method of determining correction, which is equally accurate and often more convenient, is to filter a portion of the tanning solution through the Berkefeld candle till optically clear, which can generally be accomplished by rejecting 300 or 400 c.c. and returning the remaining filtrate repeatedly; and at the same time to evaporate 50 c.c. of clear filtrate obtained by the method for which correction is required, when the difference between the residues will be the correction sought.

Note.—It is obvious that an average correction must be obtained from at least 5 determinations. It will be found that this is approximately constant for all materials, and amounts in the case of S. and S. 605, 150 c.c. being rejected, to about 5 mgr. per 50 c.c. and where 2 grm. of kaolin are employed in addition, to 7½ mgr. The kaolin must be previously washed with 75 c.c. of the same liquor, which is allowed to stand 15 minutes and then poured off. Paper 605 has a special absorption for a yellow colouring matter often contained in sulphited extracts.

It is proposed that the Commission should be asked to determine average corrections for the more important methods of filtration and report at an early date.

7. *Detannisation.*—The hide-powder employed shall be of a woolly and not granular texture, thoroughly delimed, preferably with hydrochloric acid, and not requiring more than 5 c.c. of N/10 NaOH or KOH to produce a permanent pink with phenolphthalein on 6½ grm. of the dry powder suspended in water (4); and the detannisation shall be conducted in the following manner:—

The moisture in the air-dried powder is determined and the quantity equal to 6.5 grm. actual dry hide-powder is calculated, which will be practically constant if the powder be kept in an air-tight vessel. Any multiple of this quantity is taken according to the number of analyses to be made, and wet back with approximately ten times its weight of distilled water*; 2 grm. per hundred of dry powder of crystallised chromic chloride ($\text{Cr}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$)† is now dissolved in water and made basic with

* Very woolly powders require slightly more than 10 times their weight of water.

† Kahlbaum.

0.6 grm. Na_2CO_3 by the gradual addition of 11.25 c.c. of N/1 solution, thus making the salt correspond to the formula $\text{Cr}_2\text{Cl}_3(\text{OH})_3$ (5). This solution is added to the powder, and the whole churned slowly for 1 hour. In laboratories when analyses are continually being made it is more convenient to use a 10 per cent. stock solution, made by dissolving 100 grm. of $\text{Cr}_2\text{Cl}_3 \cdot 12\text{H}_2\text{O}$ in a little distilled water in a liter flask, and very slowly adding a solution containing 30 grm. of anhydrous sodium carbonate, with constant stirring, finally making up to mark with distilled water and well mixing. Of this solution 20 c.c. per 100 grm. or 1.3 c.c. per 6.5 grm. of dry powder should be used.

At the end of one hour the powder is squeezed in linen to free it as far as possible from the residual liquor, and washed and squeezed finally with distilled water, until on adding to 50 c.c. of the filtrate, 1 drop of 10 per cent. K_2CrO_4 and 4 drops N/10 AgNO_3 , a brick-red colour appears. Four or five squeezings are usually sufficient. Such a filtrate cannot contain more than 0.001 grm. of NaCl in 50 c.c.

The powder is then squeezed to contain 70-75 per cent. water, and the whole weighed. The quantity Q containing 6.5 grm. dry hide is thus found, weighed out and added immediately to 100 c.c. of the unfiltered tannin infusion along with $(26.5 - Q)$ of distilled water (6). The whole is corked up and agitated for 15 minutes in a rotating bottle at not less than 60 revolutions per minute (7). It is then squeezed immediately through linen, 1 grm. of kaolin added to the filtrate, stirred and filtered through a folded filter of sufficient size to hold the entire filtrate, returning till clear, and 60 c.c. of the filtrate is evaporated and reckoned as 50 c.c. or the residue of 50 c.c. is multiplied by $\frac{5}{3}$. The non-tannin filtrate must give no turbidity with a drop of a 1 per cent. gelatin 10 per cent. salt solution (8).

8. *The Analysis of Used Liquors and Spent Tans.*—This shall be made by the same methods as are employed for fresh tanning materials, the liquors or infusions being diluted, or concentrated by boiling *in vacuo*, or in a vessel so closed as to restrict access of air, until the tannin matter is, if possible, between 3.5 and 4.5 grm. per liter, but if from any cause it is impossible to reach this concentration the weight of hide-powder used shall not be varied from $6\frac{1}{2}$ grm. in consequence.

The results shall be reported as shown by the direct estimation, but it is desirable that in addition efforts shall be made by determination of acids in the original solution, and in the non-tannin residues, to ascertain the amount of lactic and other non-volatile acids absorbed by the hide-powder, and hence returned as "tanning matters." In the case of tans it must be clearly stated in the report whether the calculation is on the sample with moisture as received, or upon some arbitrarily assumed percentage of water; and in that of liquors whether the percentage given refers to weight, or to grm. per 100 c.c.; and in both cases the specific gravity shall be reported.

In carrying out the above resolutions, this method may be brought into immediate use from that date, but *becomes compulsory for all members of the I.A.L.T.C. eight weeks after this publication, viz. September 15, 1907.*

Analyses carried out according to the findings of the Commission must be marked on the report—"Analysed according to the resolutions of the I.A.L.T.C. of September 19, 1906."

The resolution of Müller, "That reports of analyses shall only be sent out on a mean of at least two separate analyses which closely correspond," should be again carefully noted.

I take this opportunity of expressing to all the members and workers in the Commission the thanks and appreciation of the whole I.A.L.T.C. for their unselfish and painstaking work.

PROF. DR. H. BECKER,
President of the I.A.L.T.C.,
on behalf of the Executive Committee.

FRANKFURT ON MAIN, July 11, 1907.

OFFICIAL METHOD OF THE AMERICAN LEATHER CHEMISTS ASSOCIATION FOR TANNIN ANALYSIS.

I. *Crude Materials.*

1. *Moisture Determination.*—Upon receipt of the sample, grind promptly and dry 10 grm. in the manner and for the period specified for evaporation and drying in extract analysis.

2. *Preparation of Sample for Extractions.*—Sample must be

dried at a temperature not exceeding 60° C., and then ground to such a degree of fineness that the entire sample will pass through a sieve of 20 meshes to the inch (linear).

3. *Amount of Sample and Proportion of Water for Extraction.*—For fresh materials the amount of sample and proportion of water for extraction should be such as to give between 0.35–0.45 gm. tannin per 100 c.c. of solution. For spent materials this proportion should be approximated as closely as practicable.

4. *Extraction of Sample.*—Extraction should be conducted in a form of apparatus that permits the removal of the extractive solution from the influence of sustained high temperature, and shall be continued till a portion tested with gelatin salt solution fails to give a precipitate. At least 400 c.c. of the first portions of extractive solution should be removed and not subjected to further heating. A thin layer of cotton must be used in order to prevent fine material passing over.

5. *Analysis.*—After extraction and dilution, solutions must be heated to 80° C., and analysis conducted as per Official Methods for Extracts. In case of weaker dilutions than the Official Method specifies, the amount of hide-powder must be reduced in proportion to the reduction of tannin.

Ten gm. of the air-dried sample should be dried as in (1) to determine moisture content of the portion extracted, and the analysis calculated and reported upon a "dry" basis. The tannin in fresh materials should also be reported on the basis of the moisture content of the sample "as received."

II. Analysis of Extracts

6. *Amount and Dilution for Analysis.*—Fluid extracts must be allowed to come to room-temperature and weighed in stoppered weighing bottle. Such quantity shall be taken as will give from 0.35–0.45 gm. tannin per 100 c.c. of solution, dissolve in exactly 900 c.c. of distilled water at 80° C., and make up to mark after standing not more than 20 hours, nor less than 12 hours. Temperature must not go below 20° C.

7. *Total Solids.*—Thoroughly mix solution, pipette 100 c.c. into tared dish, evaporate and dry as directed under "Evaporation and Drying."

8. *Soluble Solids.*—To 1 gm. of kaolin in a beaker add 75 c.c. of solution; stir and pour on 590 S. and S. 15 cm. pleated

filter paper ; return filtrate to paper for one hour, keeping filter full. At end of hour pour solution from filter or remove with pipette. Bring 800 c.c. of solution to 20° C. ; refill the filter with this solution and begin to collect filtrate for evaporating and drying so soon as filtrate comes *clear*. Keep filter full. Evaporate and dry the first 100 c.c. of filtrate, as per "Evaporation and Drying."

Funnels and receiving vessels must be kept covered during collection of filtrate for evaporation.

9. *Non-Tannins*.—A quantity of hide-powder sufficient for the number of analyses to be made shall be prepared in the following manner: Digest with twenty-five times its weight of water till thoroughly soaked. Add 3 per cent. of chrome alum in solution. Agitate by either shaking or stirring occasionally for several hours and let stand over night. Wash by squeezing through linen, continuing the washing until the wash water gives no precipitate with barium chloride. Squeeze the hide, using a press if necessary, so that the wet hide will contain between 70 and 75 per cent. of water. Use approximately 20 gm. of wet hide for moisture determination. Add to 200 c.c. of the original solution such quantity of the wet hide as represents from 12 to 13 gm. dry hide. Shake for ten minutes in some form of mechanical shaker and squeeze immediately through linen. Add 2 gm. kaolin to the filtrate, stir and filter through folded filter (No. 1 F Swedish, recommended) of size sufficient to hold entire filtrate, returning till clear. Evaporate 100 c.c. of the filtrate. The weight of the residue must be corrected for the dilution caused by the water contained in the wet hide-powder.

The non-tannin filtrate must not give a precipitate with a 1 per cent. gelatin 10 per cent. salt solution.

10. *Tannin*.—The tannin content is shown by the difference between the soluble solids and the corrected non-tannin.

III. Analysis of Liquors.

11. *Dilution*.—Liquors must be diluted for analysis so as to give as nearly as possible 0.7 gm. solids per 100 c.c. of solution.

12. *Total Solids*.—To be determined as in Extract Analysis.

13. *Soluble Solids*.—To be determined as in Extract Analysis.

14. *Non-Tannins*.—To be determined by shaking 200 c.c. of solution with an amount of wet chromed hide-powder, containing 70 per cent. to 75 per cent. moisture, corresponding to an amount of dry hide-powder shown in the following table:—

Tannin Range per 100 c.c.	Dry Hide-Powder per 200 c.c.
0.35-0.45 gm.	8-10 gm.
0.25-0.35 gm.	5-8 gm.
0.15-0.25 gm.	2-5 gm.
0.00-0.15 gm.	0-2 gm.

Solutions to be shaken for non-tannins as in Extract Analysis; 100 c.c. must be evaporated as in Extract Analysis.

IV. Evaporation and Drying.

15. *Evaporation and Temperature*.—All evaporations and dryings shall be conducted in the form of apparatus known as the "Combined Evaporator and Dryer," at a temperature not less than 98° C. The time for evaporation and drying shall be 16 hours.

16. *Dishes*.—The dishes used for evaporation and drying of all residues shall be flat-bottom glass dishes of not less than 2½ inches diameter nor greater than 3 inches in diameter.

Notes on Official Methods.

1. Variations from the prescribed strength cause the largest errors where difficultly soluble tannins such as those of quebracho are present, as the more dilute the solution the larger proportion is dissolved. In this case also differences of temperature have the largest effect on the result, since these difficultly soluble tannins are readily brought into solution at higher temperatures, thus causing a lessening of the so-called "insolubles" and an increase of tannins. It must be remembered that a large proportion of these insolubles are really of the nature of tannins, and under suitable conditions contribute to make leather. The writer has shown that skin can be thoroughly tanned by agitation with the insolubles of quebracho extract merely suspended in water.

It has been found that with most extracts a slightly larger quantity is brought into solution if the whole of the water used is at boiling temperature, though the difference between this and the American prescription of 80° C. is quite negligible. The same may be said with regard to the question of cooling rapidly

or slowly to the required temperature ; the International method has the advantage of much greater rapidity of execution, and in cold weather there is less danger of cooling during the night below the prescribed temperature, which would lead to slightly lower results ; but with matters like quebracho, which contain much difficultly soluble tannin, the separation with slow cooling is probably slightly better, and the filtration easier. With materials containing ellagitannic acid, the separation of bloom is greater the higher the temperature, and the longer the solution is allowed to stand.

2. It is important that the greater part of the tannin of solid materials should be removed at a low temperature, and not afterwards subjected to heat, which especially with bloom-giving materials precipitates a portion of the ellagitannic acid as bloom. Boiling has also been shown to destroy tannin in many catechol tannins, and it is probable also that at higher temperatures a portion is fixed by the fibre or proteids of the tannin material. The reason for restricting extraction to 1 liter is principally to increase uniformity and save time, and with careful extraction and fine grinding all tannin available for the tanner can be extracted with this quantity, though by more prolonged extraction a slightly larger amount of solubles and a trace more of the difficultly soluble tannins is obtained, but the troublesome and tedious concentration of the later and weaker runnings is involved.

3. By the American "contact filter" method it is in many cases impossible to obtain optically clear (i.e. brilliant) filtrates, and it is assumed that by uniformity of operation, a uniform degree of opalescence can be obtained, and consequently a concordant if empirical amount of "insolubles." It has, however, been shown in the author's laboratory that in some cases a solution may appear transparent to transmitted light, and yet contain as much as 10 per cent. of matter which must be filtered out before a brilliant solution is obtained ; while 5 per cent. is not uncommon ; and as filter paper cannot be obtained of uniform closeness, and trifling differences of temperature and manipulation affect the fineness of division of the opalescent material, no real concordance of result can be obtained. The International Association has therefore determined that actually brilliant solutions must be obtained, and it has been shown that such solutions cannot contain more than at most a few tenths per cent. of matters which can be removed by further filtration.

With most extracts brilliant solutions can be obtained by filtration, repeated if necessary, through the Berkefeld candle, which, if the first 200 c.c. be rejected, does not absorb any appreciable quantity of soluble tannin, but in some cases, such especially as hemlocks and quebrachos, it is necessary to use Schleicher and Schull's "extra-hard" paper, with or without the addition of kaolin, and this paper has an appreciable absorption even for soluble tannins, which must be allowed for by the method given in the text. Most other filter papers with or without kaolin have an appreciable though smaller absorption, which should be similarly corrected.

4. A granular powder * gives equally concordant results, and absorbs a lesser quantity of non-tannins, but as woolly powders are mostly in use, it has been thought best to prescribe their universal employment, although their surface absorption is somewhat greater. The degree of original acidity of the powder is of considerable importance, as excess of acid lessens the amount of chrome taken up, and makes the chromed powder more acid, with the result of greater absorption of non-tannins. It is easy, for instance, to make a granular powder as absorbent as a woolly one by additional acidification, and it will be found that most of the slight want of concordance in results of different powders are due either to marked differences of texture, or to irregular acidification.

5. The use of basic chrome chloride† in place of normal chrome alum has the advantage of chroming more rapidly and fully, and it is believed that the results are more uniform and less affected by slight differences in acidity of the original powder, but the particular chrome salt used has only a minor influence on the result. Chlorides have the advantage over sulphates of being easily estimated by N/10 silver nitrate, which facilitates the determination of the acidity of the powder and the sufficiency of the washing, which is of great importance. Strictly taken, it is impossible to wash a powder chromed with normal chrome alum till it will give no precipitate with barium chloride, as slow hydrolysis of the basic chrome sulphate fixed in the powder continues for an almost unlimited time, and there is no simple test which shows when the sulphates have been reduced to a negligible amount.

Bennett, Journ. Soc. Chem. Ind., 1907, p. 455.

† Procter and Bennett, Journ. Soc. Chem. Ind., 1906, p. 1203; 1907, p. 79.

6. The method of determining moisture* prescribed by the International Association is believed to be more convenient in practice, and equally accurate with the American method of direct drying, and if both methods are carried out properly, the effect of any small difference on the analysis is within the limits of negligible error. In proof of this, it may be pointed out that a 1 per cent. error in moisture determination would only cause an error of 0.05 per cent. of tannin in a 30 per cent. extract. Small errors in the International method may be caused by excess of solubles in the original hide-powder, or by loss of powder by careless manipulation, but are almost compensated by the larger amount of water which must then be added to make up $(26.5 - Q)$. On the other hand the American method is subject to at least equal errors from the impossibility of insuring an absolutely uniform sample of the moist powder, and the danger of driving off water of combination in the drying, especially if the powder is not thoroughly air-dried before submitting it to a high temperature, which from the time involved, is impossible in practice.

7. The time or violence of the agitation makes no practical difference in the result so long as it is sufficient to insure the complete removal of the tannin, as shown by the salted gelatin test, and it is obvious that any other equivalent form of shaking machine, or even of hand shaking can be used without affecting the results. In fact the words "or other equivalent method of agitation" were inserted in the report, but inadvertently omitted in printing. Earp's statements with regard to the inefficiency of the gelatin test have no foundation in fact, if the test is properly carried out.

8. No definite instructions for drying are issued by the I.A.L.T.C. beyond the statement that residues must be dried till [†]constant, and that the temperature must not exceed 105° C. in air, or 100° C. *in vacuo*, since it is felt that the subject requires closer investigation before any more detailed direction is given. It is believed by the Commission that drying *in vacuo* is the more perfect method, but the cost of the apparatus prevents its being made compulsory in all laboratories. The air-oven requires great care in its use and a good thermostat to secure uniform temperature. The Reed combined evaporator and dryer† is very con-

Procter and Bennett, Journ. Soc. Chem. Ind., 1906, p. 1203.

† Journ. of Am. Lea. Chemists' Assoc., 1906, p. 32.

venient, and gives uniform results, but involves 16 hours drying, and is open at least to the theoretical objection that change and oxidation may take place in some extracts from slow evaporation and long continued heating.

9. The detannisation of liquors requires further investigation. The amounts of hide-powder prescribed by the American Association (par. 11) have not proved in all cases sufficient for a complete detannisation, and it was thought best by the International Commission to prescribe a uniform amount of powder with a view to concordance. It is clear, however, that, especially in presence of large quantities of non-tannins of an acid character, the determination of small amounts of tannin cannot be regarded as of great accuracy. (Compare p. 197.)

SECTION XIV.

VOLUMETRIC METHODS OF ESTIMATING TANNINS.

IN recent times volumetric methods have been almost entirely superseded by gravimetric methods with hide-powder, but there are still cases in which they may be employed with advantage, and it is quite possible that in the future they may again assert their importance for general use. Several of the older methods are briefly referred to in Section X. Where only one or two analyses are to be made at one time, the preparation and adjustment of solutions are much more tedious than gravimetric analysis; but where a number of successive titrations are required, volumetric methods are considerably more rapid. The most important of the methods hitherto in use is that of Löwenthal. It has the advantage that it can be applied direct to solutions, however dilute, without the need for previous concentration, and if gelatin precipitation is used, it is much less affected by the presence of gallic or other fixed acids than the hide-powder method, and is therefore well adapted for the analysis of weak and waste liquors for technical purposes, for the systematic testing of spent tans, and for the analysis of sumach, and myrobalans, which contain much gallic acid, which,

in the gravimetric method, is wholly or partially estimated as "tanning matter."

The method of titration with permanganate in presence of indigo was originally published by Löwenthal in the '*Journ. f. Prakt. Chem.*,' in 1860,* who at first thought that only tannins were oxidised. It was, however, soon shown that gallic acid and other non-tanning substances present were also oxidised, and Neubauer † proposed, after determining the total astringents, to remove the tannin by animal charcoal, and by a second titration to determine the tannin by difference. Löwenthal soon afterwards‡ described the method of precipitation with gelatin in presence of salt and acid, and at the same time pointed out that the tannin might also be removed by the use of hide-powder, as in Hammer's method (p. 173). Some years later, it was shown by Simand that the precipitate of tannin and gelatin was to some extent soluble in the salt and acid solution employed, so that the non-tannins came out always too high, and that the error became greater as weaker solutions were employed. He showed that this solubility might be calculated in any given case by determining the non-tannins with two different strengths of tannin solution, and finding what deduction for solubility would bring them into constant ratio to the tannin present; but as this complicated the analysis, he preferred to absorb the tannin with hide-powder, or with decalcified bone or horn-piths, ground and purified in the same way, and preferably dehydrated with alcohol.

It was not recognised at that time that these materials absorbed material quantities of gallic acid when present, and therefore introduced an error in the opposite direction, a fact pointed out by Procter in 1876;§ and Simand's suggestion was generally adopted. Procter || endeavoured to overcome the

* *ibid.* p. 150.

† *Zeitsch. f. Anal. Chem.*, 1871, p. 1.

‡ *Zeitsch. f. Anal. Chem.*, 1877, pp. 33, 201; 1881, p. 91.

§ *Proc. Newcastle Chem. Soc.*, 1876, p. 214; *Journ. Soc. Chem. Ind.*, 1886, p. 81; 1887, p. 94.

|| The method is as follows: To 50 c.c. of the infusion 28.6 c.c. of a gelatin solution of 2 grm. per 100 c.c. is added. After shaking, the mixture is saturated with salt, which brings the volume up to 90 c.c., and 10 c.c. of dilute sulphuric acid (containing 1 vol. of concentrated acid in 10) and a teaspoonful of pure kaolin are added. It is best to do this in a flask in which it can be well shaken, after which filtration may be at once proceeded with, although it is safer to let it stand an hour or two (the flask may be cleansed with caustic soda solution). 10 c.c. of this filtrate (= 5 c.c. of the original infusion) are employed for titration.

solubility of the tannin precipitate by saturating the solution with salt,* which precipitated the tannin much more perfectly, as well as nearly the whole of the gelatin, and at the same time he introduced the use of kaolin, which assists the precipitation, and the production of a clear filtrate in a very marked degree. It was, however, pointed out by Hunt† that under these conditions a marked amount of gallic acid was precipitated from liquors containing it, and he went back to a proportion of salt even less than that originally used by Löwenthal, but retained the use of kaolin or barium sulphate. Although Hunt's results can only be rigidly correct by a compensation of errors, his method yields, perhaps, the nearest approximation which can be obtained in the case of materials containing gallic acid, and if it were worth while to strive for greater accuracy in a method which is at best only approximate, it would not be difficult to apply Simand's correction in a simple form by rigidly adhering to constant quantities.

Turning from the separation of tannin to the details of the titration process, it must be remarked that Löwenthal himself pointed out that the function of the indigo was not merely that of an indicator, but that it also acted as a regulator, preventing the oxidation of matters of a more stable character than itself, and that therefore, it was necessary to have it present in considerable excess. It was also found that the quantity of permanganate consumed by a given amount of tannin varied materially, according to the rate at which the permanganate was added, rendering all attempts to fix a definite ratio illusory. Kathreiner, who very carefully investigated the method,‡ endeavoured to render the results more constant by prescribing a fixed time for the titration to occupy; and von Schroeder§ proposed that the permanganate should be added 1 c.c. at a time at definite intervals of 5–10 seconds. It was afterwards shown by Procter|| that what really made the difference was the speed of *mixture*, and that therefore the result was as much influenced by the vigour of the stirring as by the rate of addition, and that

* Journ. Soc. Chem. Ind., 1884, p. 82.

† Ibid., 1885, p. 263.

‡ Ding. Polyt. Journ., 1878, ccxxv. p. 481.

§ 'Bericht der Commission zur Feststellung einer einheitlichen Methode der Gerbstoffbestimmung, Cassel, 1885.

|| Journ. Soc. Chem. Ind., 1886, p. 79.

in this respect the "1 c.c." method was much more easily affected than the ordinary "drop method."

The explanation of the variation is a simple one. The oxidation in the Löwenthal process should be limited to indigo, and bodies more oxidisable than indigo, but there exist both ready formed in liquor, and among these oxidation products, many substances which, in the absence of indigo, will readily reduce permanganate. When the latter is added rapidly, and with insufficient stirring, it destroys the indigo and tannin in contact with it, and then proceeds also to oxidise the other matters present, although in other parts of the beaker indigo and tannin still exist. Thus more permanganate is reduced than corresponds to the indigo and tannin, and this is especially so towards the end of the process, when very little of either remains. The more slowly the permanganate is added, and the more vigorously it is stirred, the more closely it will approximate to the theoretical quantity required merely to oxidise the indigo and tannin.

A much more valuable suggestion than that of the "1 c.c." method was, however, made by von Schroeder,* which has since been universally adopted. It is obvious that if in every case the permanganate solution be standardised against one of pure tannin, under precisely the same conditions under which the analysis is made, any variations dependent on the rate of mixture will mutually compensate each other; and this method would have been universally adopted, but for the impossibility of obtaining really pure tannin. Von Schroeder showed that the principal impurity in the purest commercial tannins is gallic acid, which is oxidised similarly to tannin in presence of indigo, but consumes slightly more permanganate, and therefore influences but little the amount of permanganate consumed by such a tannin. According to his experiments, 1 grm. of the purest commercial tannins was equal in reducing power, on the average, to 1.05 grm. of theoretically pure, and he therefore proposed to multiply the amount actually weighed out by this figure. Procter suggested the employment of pure crystallised gallic acid as a standard, which, perhaps, hardly received the attention it deserved, since it is oxidised in the same way as tannin in presence of indigo, and is easily obtained in a pure

* Loc. cit. See Note §, p. 225.

state. 1 grm. of crystallised gallic acid is equivalent to about 1.25 grm. of "pure tannin," as calculated by von Schroeder's data, but further experiments are required to fix the quantity with complete accuracy.

The values obtained by this method are only correct for gallotannic acid, and little is known of the proportionate consumption of permanganate by other tannins. For a long time, a statement of Oser's that oak-bark tannin consumed 1.5 times as much permanganate as gallotannic acid was accepted as a basis of calculation, but after the introduction of the hide-powder gravimetric method it was found that the relation between the two varied irregularly, even for the same kind of material,* and if it is desirable to calculate even approximate percentages in a series of determinations of any other tannin than gallotannic acid, the only way is to determine a factor at the time, by a sufficient number of simultaneous gravimetric analyses (p. 212) of the same material.

The working details now adopted in the Leeds University Laboratory are as follows. The solutions required are:—

1. Pure potassium permanganate, 0.5 grm. per liter. As very weak solutions keep badly, it is best to make up one of 5 grm. per liter, and dilute when wanted. The exact strength of the permanganate is not important so long as it is constant through a series of experiments.

2. Pure indigo carmine (potass or sodium sulphindigotate), 5 grm., and concentrated H_2SO_4 , 50 grm. per liter. This must be filtered, and should give a pure yellow free from any trace of brown where oxidised with permanganate; 25 c.c. of this solution should equal about 30 c.c. of the permanganate, and, if necessary, must be diluted to that strength.

As it is frequently difficult to obtain indigo carmine of satisfactory purity, the use of synthetic indigo, as suggested by Rawson, may be recommended. 1 grm. "indigo pure B.A.S.F." is dissolved by heating to a temperature of 75–80° C. with 25 c.c. of sulphuric acid S.G. 1.84 for 1 hour, stirring occasionally with a glass rod. After cooling, 25 c.c. more acid are added, and the whole made up to 1 liter.

3. Solution of pure tannin, 3 grm. to 1 liter.

Since absolutely pure tannin cannot be obtained, the follow-

* 'Gerber,' 1887, p. 3.

ing method is adopted: A sample of the purest obtainable tannin (not less than 90-95 per cent. pure by hide-powder) is preserved air-dry in a well-stoppered bottle, and the moisture carefully determined. The principal impurity is gallic acid, which acts on permanganate like tannin, but reduces somewhat more, and 1 part of such tannin, calculated to dry weight, is equal on the average to 1.05 parts of pure tannin. Hence it is easy to calculate a quantity of the air-dry tannin equal in permanganate value to 0.3 grm. of pure tannin, and this is weighed out when required and made up to 100 c.c. The moisture varies very little, but it is well occasionally to re-determine it and calculate afresh.

Titration.—25 c.c. of the indigo-carmin solution is mixed in a beaker with about $\frac{3}{4}$ liter of tap water, and the permanganate added drop by drop from a glass-tapped burette till a pure yellow is obtained, the liquid being stirred steadily the whole time. A disc stirrer or a glass rod bent several times back and forward, is to be preferred to a plain rod; or some method of mechanical stirring may be adopted. The dropping should be always as nearly as possible at a similar rate for each experiment, and should be slower towards the end of the titration. It is convenient to keep a second beaker titrated to a pure primrose yellow as a standard test. Titrations may be accurately performed by artificial light, but usually differ slightly from those by daylight, and hence the light should not be varied in the course of an analysis. For daylight work Kathreiner recommends the use of a white basin instead of a beaker. The permanganate solution is allowed to drop in, with constant stirring, till the pure yellow liquid shows a faint pinkish rim, most clearly seen on the shaded side. This end reaction is of extraordinary delicacy, and is quite different to the pink caused by excess of permanganate, being an effect common to all pure yellow liquids. The titration is done at least twice, and the average taken; $\frac{3}{4}$ liter of water and 25 c.c. of indigo are then taken as before, and 5 c.c. of the tannin solution are added and similarly titrated repeatedly. Deducting amount required for the indigo, the remainder is that consumed by the tannin, which should not at most exceed two-thirds of that required by the indigo. A similar titration is made with the tannin infusion to be examined, of which such a number of cubic centimeters is employed as will consume about

the same quantity of the permanganate as the standard tannin solution. The value of the total astringent is then calculated in terms of tannin.

Since tanning matters contain astringents which are not taken up by the hide, but which are oxidised by permanganate like tannins, it is in most cases necessary to remove the tannin from a portion of the infusion, and to repeat the titration to determine the non-tannin.

Detannisation by Hide-Powder.—This may be done by the same method as is used when the tannin substance is determined gravimetrically. This is desirable where liquors containing tannins other than gallotannic acid are to be estimated, since it is found that the weight calculated as "pure tannin" (gallotannic acid) is in many tanning materials very different from that determined gravimetrically. This fact may be taken advantage of in recognising the classes of tannins which are contained in an extract. If a gravimetric determination is made at the same time, a factor may be calculated which will give results on other samples of the same material closely approximate to those obtained directly by gravimetric analysis.

Detannisation by Gelatine. Hunt's modification.—This is generally applicable, and especially so to liquors containing gallic acid, of which it removes less than hide-powder. It is also much more rapid of execution than detannising by hide-powder.

Solutions required.—1. Pure gelatine, 2 grm. per 100 c.c.

2. Saturated solution of NaCl containing 50 c.c. of concentrated H_2SO_4 per liter.

Precipitation.—To 50 c.c. of the liquor (of about the strength required for the hide-powder process) is added 25 c.c. of the gelatin solution and 25 c.c. of the salt solution, and about a teaspoonful of kaolin or baric sulphate, and the whole is well shaken for five minutes and filtered. This filtrate, which should be perfectly bright, is titrated for non-tannin by the Lowenthal method, double the volume being taken which was employed for determination of total astringents, and the result is deducted before calculating the tanning value.

Calculation of Löwenthal's Estimations.—If only the tannin is required, the result is best obtained by a simple proportion sum—If 3 grm. per liter of pure tannin consumes a c.c. of perman-

ganate, and the solution tested b c.c. (after deducting that consumed by the indigo and non-tannins), the solution will contain $3b/a$ grm. of tannin per liter. If any other strength than 3 grm. per liter has been used for the standard, or it has been determined by gravimetric analysis, the quantity used or found must be substituted for 3. In a similar way the non-tannin permanganate may be reckoned to its tannin value, and reduced to gallic acid, by division by 1.35, but the value will include beside real gallic acid, all other easily oxidisable matters present in the solution. The non-tanning oxidisable matter of sumacs differs in many respects from pure gallic acid.*

Estimation of Tannin by Jean's Method.—F. Jean estimates tannins with a solution of iodine in presence of sodium bicarbonate. The method is described in his "Industrie des Cuirs et Peaux," p. 116, and with some modifications and improvements in Wiss. Beilage der Ledermarkt I. (1899-1900) p. 113. The method is capable of giving good results, at least with gallo-tannic acid, but does not seem to have marked advantages in either accuracy or facility of execution over the Löwenthal method.

The iodine solution is made by rubbing up 3.77 grm. of iodine in a mortar with a little water and 5 or 6 grm. of potassium iodide, and making up to 1 liter. Tannin and gallic acid solutions of 1 grm. per liter are used for standardizing. 10 c.c. of the tannin solution, and 5 c.c. of a saturated solution of sodium bicarbonate are introduced into a small beaker of 5 or 6 cm. in diameter, and with a mark to contain 50 cm. The iodine solution is now added drop by drop from a burette, constantly stirring the liquid with a glass rod, until about 9 cm. have been added. A drop of the liquid is then taken on a glass rod and spotted on to filter paper which has been rubbed over with starch, the spotting being so managed that only the drop and not the rod itself comes in contact with the paper. If iodine is present in excess a grey spot with blue edges will be produced upon the paper, and if this is not the case more iodine solution must be added until the blue edges appear. The glass is then filled up to the 50 c.c. mark with distilled water, and the spotting repeated. If no colour appears, the right quantity of iodine has

* Commercial gelatine often contains sulphites and other matters which reduce permanganate, and which must be determined, if present, by a blank experiment.

not yet been exceeded, and 5 or 6 drops of iodine solution must be given before this occurs, the end of the titration being marked by the re-appearance of the blue ring. As the coloration is somewhat fleeting, the first appearance of this ring must be taken as the end point. 10 to 10.5 c.c. of iodine solution should be required for the 10 c.c. of tannin solution, and if this is not approximately the case with pure tannin, the iodine solution must be diluted or strengthened as required. In working with gallic acid about 3 c.c. more of iodine solution will be required than for the same strength of tannin, and in titrating unknown solutions the quantity or strength of the solution must be varied so as to make the amount of iodine solution employed as nearly as possible the same as that with the pure tannin. A correction is required for the amount of iodine solution which must be added to 5 c.c. of sodium bicarbonate solution diluted to 50 c.c. with distilled water before the blue reaction is produced. This is determined by a blank experiment, and amounts approximately to 0.4 cm., which must in each case be deducted from the iodine solution used for titration. In order to separate tannin and gallic acid Jean employs egg-albumen, prepared by rubbing 2 grm. of dry albumen with a sufficient quantity of white glycerine of 28-30° Baumé to form a thick paste. The mixture is allowed to stand for half an hour and then filled up with tepid water to the volume of a liter. A few pieces of camphor are added as an antiseptic, and the neck of the flask is closed with a plug of cotton wool wetted with a few drops of formalin. In order to precipitate the tannin, 50 c.c. of the tannin solution are introduced into a 100 c.c. flask. 15 c.c. of the albumen solution and 20 grm. of common salt are added, shaken up, filled up to the mark with water, and again shaken to complete the solution of the salt. The solution is filtered through a small filter, the first few centimeters being rejected and 20 c.c. (equal to 10 c.c. of the original solution) are run into a porcelain basin, slightly acidified with acetic acid and heated to boiling to precipitate the excess of albumen. It is then filtered through a small pleated filter, the precipitate well washed, and the filtrate and washings which amount to 30 or 35 cm. are titrated with iodine exactly in the method described. A further correction, which usually amounts to about 0.7 cm. is required for the iodine absorbed by the albumen, which is also determined by a blank experiment. Tannin materials which contain water-

soluble starchy compounds must be extracted with alcohol in order to avoid the influence of the starch. If sulphites are contained in extracts, which is now very commonly the case, they must be removed by acidification with hydrochloric acid and evaporation before making the estimation. The extraction of tanning materials is similar to that used for the gravimetric method, but the solution is only about one quarter the strength, and if tolerably clear does not require filtration, so that in many cases a simple procedure of extraction may be adopted.

The Parker-Payne Method of Tannin Estimation.—In 1904,* a new method for the analysis of tannin and tanning materials was described by Dr. J. G. Parker and Mr. E. E. Munro Payne, which excited very considerable interest, and which was based on the attractive idea of determining the total acidity of a liquor including the tannins, and afterwards detannising and estimating the tannins by difference. It is in a sense an extension of the Procter method for estimating acidity with lime water, p. 243, and depends on the precipitation of the tannins and allied bodies with a solution of sugar-lime or of barium hydroxide, filtering and titrating back the excess of lime or baryta with standard acid and phenolphthalein. The end-reaction is very sharp, and the process at first sight an extremely promising one, but unfortunately on investigation sources of error appear which it is difficult or impossible to overcome. The details of the process as originally published are as follows:—

300 c.c. of N/5 calcium hydroxide solution is added in a stoppered cylinder to 200 c.c. of the clear liquor to be examined, which must contain approximately the same quantity of tannin as is required by the I. A. L. T. C. method for the hide filter (about 4 grm. per liter). The mixture is shaken repeatedly and allowed to stand for about four hours with occasional shaking. 100 c.c. are filtered off and the amount of alkali is titrated back in presence of phenolphthalein. This amount multiplied by 5 and deducted from the 300 c.c. of hydroxide solution employed gives the volume of N/5 calcium hydroxide solution which has been absorbed by 200 c.c. of the original liquor. This figure is termed by the authors of the paper the "total absorption value." Since this obviously includes the value of all acids present in the liquor, the authors proceed to remove tannin and to repeat the

determination. As a precipitant, a mixture of gelatin and gelatin-peptones is used, which the authors call "collin," and which is prepared as follows:—

60 grm. of a good commercial gelatin, which it is stated must be produced from skin, is soaked in about 500 c.c. of distilled water, and warmed until dissolved. 120 c.c. of N/1 caustic soda is added, and the mixture is heated on a water-bath for twenty minutes at 90°C ., and is then filtered through linen. The cooled solution is made up to accurately 500 c.c., and 100 c.c. are titrated with N/1 hydrochloric acid and phenolphthalein, and the remainder is accurately neutralised with a similar quantity of N/1 acetic acid, 1 c.c. of pure chloroform is added as an antiseptic, and the neutralised portion is made up to a liter. The solution, when acidified by a dilute organic acid, is found to be a very delicate precipitant of tannic acid. To detannise the solution for analysis, 200 c.c. of the original tanning liquor is mixed with 100 c.c. of N/5 acetic acid, and 100 c.c. of the collin solution; or in case of old acid tanyard liquors which contain but little tannin, with 50 c.c. of each. The solution is filtered, and 200 c.c. of the clear bright filtrate is treated with 200 c.c. of N/5 calcium hydroxide and allowed to stand for an hour, when it is titrated as before. Deducting the amount of hydroxide neutralised by the added acetic acid, the result gives the absorption of the liquor minus the tannin, and of course the difference between this figure and the previous one corresponds to the tannin precipitated. It is not necessary to follow the authors in some theoretical considerations which they subsequently deduce with regard to so-called "colour weight," as these are founded on the radically false assumption that all tannins are simply mixtures owing their tanning value to the presence of digallic acid together with certain weight-giving substances.

Much criticism* has been devoted to the suggested method of separating the tannic acid, and it has been pointed out that the gelatin-peptones present are uncertain in their composition owing to varying degrees of hydrolysis, and that they do not necessarily precipitate tannin in the same proportions as hide-fibre. These considerations are valid as applied to a proposed method of estimating the tanning value of the solution by weighing the precipitate produced by collin, but the mixture

* Wood, Journ. Soc. Ch. Ind., 1904, p. 1071; Collegium, 1905, p. 40.

may be taken as at least a fairly good material for detanning, and the authors have suggested several other substances, and especially some of the alkaloids which may be substituted. The actual foundation of the method, however, the precipitation with calcium or barium hydroxide, rather curiously escaped criticism until it was examined in the Leeds University Laboratory,* and the assumption that it was based on the formation of a definite metallic compound had not been questioned. Very careful experiments, however, by Procter and Bennett, extending over several months, have shown that not only is the precipitate with gallic acid, and probably with most other astringent bodies, partially soluble in the precipitant, and having an alkaline reaction to phenolphthalein is estimated as a portion of the excess of calcium hydroxide, but that variable quantities of lime or baryta are carried down together with the precipitate, so that with known substances such as gallic acid, exact theoretical results are only obtained by accident. In the case of proto-catechuic acid (the acid corresponding to gallic among the catechol tannins), which is quite a possible constituent of tanning liquors, the precipitate is wholly soluble. The solution containing these partially dissolved compounds when exposed to air absorbs oxygen with great avidity, forming dark coloured precipitates, which carry down with them lime- or baryta-salts, and so increase the apparent absorption to an unknown extent. Sugar also apparently introduces unexplained chemical complications, and if the amount is increased leads to the production of a yellow and oxidisable solution; though with the quantities prescribed, the sugar-lime solution, which is preferred by the authors to barium hydroxide, is certainly the easier of the two to handle. It was hoped by Procter and Bennett that, employing barium hydroxide, and operating under strict exclusion of oxygen, more reliable results would be obtained; and it was found that the addition of some 20 per cent. of alcohol completely stopped the solubility of the precipitate in the case of gallic acid, but this unfortunately only brought into prominence the fact that variable quantities of the precipitant were carried down with the insoluble gallate, so that the results varied with every change of small details in quantities and manipulation, though they approximated to the theoretical result that all three hydroxyls of the gallic acid were saturated as well as the carboxyl group.

* Journ. Soc. Ch. Ind., 1906, p. 251.

Turning to gallotannic (digallic) acid it was found that, beside the difficulties arising from the gallic acid always present, the results varied through the hydrolysis of the compound. If the precipitated solution was filtered and titrated at once, the results approximated to the saturation of six hydroxyls with the base. Hydrolysis, however, at once set in, and the absorption gradually increased, so that no definite results could be obtained until the solution had been heated on the water-bath for an hour or more, when apparently constant results were obtained, which approximated to those of 2 molecules of gallic acid, combining with 8 equivalents of base. The investigation of some other tannins was begun, but was not carried far, as the difficulties of obtaining reliable results with these simplest and best known forms appeared to be insuperable, and the reader must be referred for details to the original paper.*

It was stated by the authors that the "total absorption value" obtained by their method exactly agreed with the results of the ordinary hide-powder analysis. It is most obvious that any such agreement could only be the result of accident, as the basis of calculation was wholly arbitrary, and, as we unfortunately know, the results of various hide-powder methods differ among themselves. The matter, was, however, investigated by Boegh †, who showed that actually in the case of the tannins of the pyrogallol group, very fair concordances were obtained, but that known catechol tannins gave results corresponding to only about two-thirds of the weight actually found. This observation is interesting, and is probably explained by the fact that, while pyrogallol has three hydroxyls capable of saturation, catechol has only two; and the reader may be reminded of the similar relation which exists between the two classes of tannins when estimated by the Lowenthal method. It is needless to point out that such a fact involves the determination of a special factor for each individual tannin, and is a complete explanation of the so-called "colour weight."

It is unfortunate that so promising a method should prove unreliable, but until radical improvements are made, the reader cannot be too strongly warned against placing any implicit confidence in its indications.

* Loc. cit.

† Nordisk Garvertidende, 1904; Collegium, 1904, p. 301.

SECTION XV.

*ESTIMATION OF COLOUR IN TANNING MATERIALS, ETC.**

THIS is often of considerable importance in the case of extracts, in which contracts are often made for deliveries equal to the buying sample in colour. It is also useful in estimating the discoloration caused by iron and other impurities.

Many forms of colorimeter have been proposed which depend on matching varying thicknesses or dilutions of a standard colour solution against the colour to be measured, but though these render excellent service where the colours are constant and identical, as in nesslerising, and the colorimetric estimation of iron, dyestuffs, etc., they are unsuitable where not only the

intensity, but the actual tint varies in the colours to be registered. Spectrometric methods are no doubt theoretically the most perfect, but at present are too complex and not sufficiently delicate for practical use, and the colour estimation of the solution is made therefore best by Lovibond's tintometer.

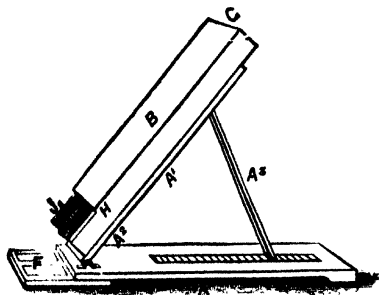


FIG. 16.

This instrument is shown in Fig. 16, and consists of an oblong box, at the upper end G of which are eye-holes for one or both eyes, while at the lower is a screen with two square openings, behind one of which can be placed a rectangular glass cell of known thickness, while behind the other is a grooved rack J in which slips of coloured glass can be inserted to match the colour of the liquid. These glasses are red, yellow, and blue, of tints carefully graduated in units and decimals of colour, and so adjusted that equal numerical quantities of the three colours will always produce a neutral tint. By suitable combinations of these, any colour can be imitated which is not brighter than that of the combined glasses,

* Parker and Procter, Journ. Soc. Ch. Ind., 1895, p. 124.

in which case a certain amount of neutral tint must be added to the colour to be matched, and noted in the result as a minus quantity. This case, however, never practically occurs in the matching of tanning materials. It is found that a set of glasses ranging from 0·1 to 20 in red and yellow, and from 0·1 to 10 in blue, is sufficient to match all tanning liquors. The ease of matching greatly depends on practice and a trained eye, and some observers never succeed, owing to defective colour vision. Matching is often greatly facilitated by the use of a coloured glass over the eyehole of the instrument (blue in the case of tanning liquors). The match should remain unaltered when this glass is removed. Light is most conveniently reflected into the instrument from a sheet of opal glass, illuminated with good daylight, and satisfactory measurements cannot be made by artificial light, or in very dark or foggy weather. The colours of opaque objects may also be measured by placing them in front of one of the openings of the instrument on the opal glass, and adding glasses to the white to effect a match; or the difference between a dyed and undyed fabric can be measured by placing one before each aperture in equal light, and compensating with coloured glasses. The colour is usually calculated on a solution containing $\frac{1}{2}$ per cent. of tanning matter, as determined by hide-powder analysis, measured in a $\frac{1}{2}$ -inch cell. It is found that within the limits of the experiment the colour varies proportionately to the strength of the solution and the thickness of the layer of liquid; so that, if a be the percentage of tanning matter in the solution employed, and b the thickness of the cell used, the value of each colour for $\frac{1}{2}$ per cent. solution in a $\frac{1}{2}$ -inch cell may be found by multiplying the observed value by the factor—

$$\frac{0.5 \times 0.5}{a \times b}$$

The most convenient strength for working with is found to be usually $\frac{1}{2}$ per cent. solution, measured in a $\frac{1}{2}$ -inch cell; but for solutions of sumach this is too weak, and for hemlock extracts and materials rich in colour a weaker solution or a thinner cell is preferable. In most cases the solution used in an analysis for tanning, usually containing about 0·4 per cent. of tanning matter, may be employed, and the results calculated to $\frac{1}{2}$ per cent. solution at will. Results may be calculated from $\frac{1}{2}$ inch to 1 cm.

cell with sufficient accuracy by multiplication by 0.8, or more accurately 0.79.*

The following method is adopted in the case of a tanning extract. The proper quantity of the extract, calculated according to analysis, is weighed into a 500 c.c. flask, and made up to 500 c.c. with distilled water as nearly boiling as possible (about a grm. of phenol having been previously added to prevent fermentation and consequent change of colour). The solution is allowed to cool, and is then carefully filtered. The filtrate must be perfectly clear or accurate measurements cannot be made. If this cannot be accomplished by ordinary means, the addition of a small quantity of kaolin is often beneficial, and has no appreciable effect on the colour. If there is the least turbidity it is most important that the cell should be shaded from diffused light, by covering all but the front with black card or velvet. It is found that where dilution is necessary the chance of error is greatly reduced by making two or more measurements, using in each case different strengths or cells, e.g. measuring 1 per cent. and $\frac{1}{2}$ per cent. solution first in a $\frac{1}{2}$ -inch cell, and afterwards in a 1-inch cell, and reducing the mean of the result to one strength. By this means it is possible to match most materials to within one-tenth of a Lovibond degree.

The measurement is made by placing the standard red, yellow, and blue glasses in the instrument, till the tint of the extract solution is exactly matched; and the values of the respective colours are read off from the numbers marked on the glasses. As, however, a combination of any equal value of all three colours makes grey or black, the smallest colour-value always combines with equal quantities of the two others to form black. It is therefore entered as black, and an amount equal to it is deducted from each of the two larger before entering. Thus if the reading were 7 red, 14 yellow and 1 blue, the result would be entered as 6 red, 13 yellow and 1 black. As light is lost by reflection from the surfaces of the standard glasses, an equal number of plain glasses must be placed with the cell, the cell itself being counted as two, though when filled with liquid this is not strictly correct. It is obvious that tintometer

The rule given, while sufficiently near for technical purposes and with small variations, is not found to hold good, if the difference of dilution or of thickness is very large.

measurement may be applied to a variety of other purposes in the tannery beside the mere matching of extracts, and especially the examination of oils and the registration of the colours of dyes may be named.

Since the animal skin has different affinity for the different colouring matters contained in tanning materials, the colour given to leather is only proportionate to the colour of the solution where the materials are identical; and it is often desirable to confirm the results of the tintometer by actual tanning experiments. The most suitable material for this purpose is calf or sheep grain, which is obtained from the tanner in the limed state after splitting and "scudding" on the beam. The skin is well washed with water, and then with a solution of 2 per cent. boric acid, and 1 per cent. pure phenol. After some hours in this solution, it is "scudded" on the grain side, on a glass plate, with a blunt brass slicker or a smooth-edged slate, to remove lime soaps, and is then preserved till required in a fresh boro-phenol solution, in which it will keep for some months. While this method of preparation answers well if properly carried out and the boro-phenol solution frequently changed, trouble is often experienced from the gradual deterioration of the skin. Apparently satisfactory results have been obtained with skins preserved with formaldehyde, and also by pickling with salt and a little formic acid, but it is obvious that if comparable colours are required, some one method must be adhered to.

For tanning, a "milk-shaker" (p. 202), or the glass churn shown in Fig. 17, is generally used. Similar results may be obtained by suspension, but in a much longer time, about 36 hours being required for tanning; and in the earlier stages the skin must be frequently moved or shaken.

Strips of the delimed sheep grain, about 8 inches by 4 inches, are cut, and, to remove the boric and phenol solution, are washed in the churn twice by shaking with distilled water, and lightly pressed out with the slicker. They are then put into the churn with a solution from the material to be used containing $\frac{1}{4}$ per cent. of tanning matter, and agitated for 20 minutes, after which the solution is strengthened to $\frac{1}{2}$ per cent., and at the end of another 20 minutes to 1 per cent. strength, and the skin is shaken with this for $1\frac{1}{2}$ hour—the tanning process thus lasting two hours.

The leather is then washed for a few minutes in distilled water, slicked out on a glass plate with a glass or brass slicker, lightly oiled with a drop of cod-liver oil, and pinned up in a dark place until dry.

This method is satisfactory, the leather drying an even colour, and repeated tests of the same material giving concordant results. The exact strength of the solution, or the length of time employed in tanning, has no appreciable effect on the colour.

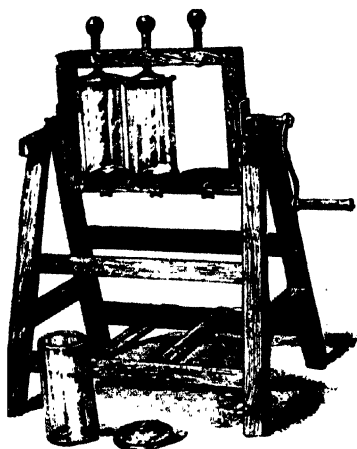


FIG. 17.

Dr. Lepetit informs the author in a private letter that he tans pelt (calf or sheep) with extract equal to about 20 per cent. of tannin on its wet weight, with 400 per cent. of water. The whole extract is added to the water at once; and the tannage lasts 12 hours. The leather is pressed through a rubber wringing machine before drying. The colour is sometimes lighter than if done in the ordinary way. If split calf pelt cannot easily be obtained thin skins may be shaved with the bate-shaver's knife

on the beam to the required thickness. The time required for tannage is somewhat longer than for sheep grain.

It is obvious that the above method of experiment may be employed for many purposes beside the mere testing of extracts and other tanning materials; as, for instance, the investigation of the effect on colour of "assistants" and additions to the tanning bath, of various methods of leaching, and of different modes of bating and preparing the skin.

SECTION XVI.

ANALYSIS OF USED LIQUORS, AND SPENT TANS.

Total Solids.—This is only important if it be desired indirectly to determine suspended matter. The liquor is well shaken and 50 c.c., or less, is measured into a basin, evaporated to dryness and dried till constant at 105° to 110° C.

In most cases the liquor may at once be filtered, either through a Berkefeld candle (p. 187), or through paper, using kaolin if necessary to get it perfectly clear. The specific gravity should always be taken with a pycnometer or hydrometer. Barkometer degrees correspond to the second and third decimals of specific gravity; thus sp. gr. $1.065 = 65^{\circ}$ Bkr.

Total Dissolved Matter.—50 c.c., or a smaller quantity of strong liquor, is evaporated to dryness in a weighed basin, dried till constant at 100° to 105° C., and weighed. In stronger layer liquors, 5 or 10 c.c. is quite sufficient. Difficulty is likely to arise from the presence of partially volatile substances, and especially of lactic acid.

Suspended Matter is determined by subtracting the "dissolved matter" from the "total solids." This calculation is only reliable in dilute solutions, where the *volume* of the suspended matter may be neglected. In other cases the suspended matter may be collected on a tared filter, weighed wet with the filter and again when dry, and the weight of dissolved matter calculated corresponding to the loss of water, and deducted from the net weight.

Ash and Organic Matter.—The residue of the "total soluble" (or "total solids") is cautiously incinerated, moistened with ammonium carbonate solution, evaporated to dryness, and cautiously heated to incipient redness to drive off ammonium salts without decomposing carbonates. The loss is total "organic matter," the residue "mineral constituents," which consist mainly of lime and may be further analysed by the methods given for the mineral matters of water, p. 45. The ash may be dissolved in excess of N/1 HCl, and titrated back, when bases found will have existed in the liquors as salts of organic acids. These neutral salts have very considerable influence on the tanning

process, and appear to be one of the principal causes of the "mellow" action of old liquors. The determination of iron in the ash is frequently of great importance, and may be made colorimetrically, p. 40.

Tanning Matter.—A portion of the filtered liquor is diluted, or concentrated, till it contains about 4 grm. of tanning matter per liter, and is analysed as described in Section XIII. by the chrome-chloride method. Where very large quantities of non-tannins are present, it is often necessary to reduce the tannins below the official strength of 4 grm. per liter. The residues of "total soluble" and "non-tannins" may be redissolved in water, and the acid in each determined (see below), and the difference, reckoned as lactic or gallic acid, as the case may be, deducted, from the tanning matter found. Where the proportion of tannin is small, great accuracy is impossible from the disturbing action of non-tannins. (Cp. p. 208.)

The results of analysis of liquors may be stated in grm., either per 100 grm. (per cent.), or per 100 c.c. (volume per cent.); but it must be made clear which is used, and the density of the liquor must always be given to render it possible to calculate from one to the other.

The Löwenthal method may also be used for tannin estimation, especially for weak and acid liquors, or where a series of determinations are required. The tannin may be reckoned in terms of gallotannic acid, when it will be always lower than the "tanning matter" determined by hide-powder; or a factor may be obtained by simultaneous hide-powder determinations of one or more of the liquors.

The Parker-Payne method has been strongly recommended, but the reader is referred to the criticism in Section XIV.

Determination of Free Acids in liquors is of great importance, both on account of their power of swelling and of removing lime, but no thoroughly satisfactory method has yet been proposed, largely owing to the impossibility of defining what is really meant by the term. Liquors may contain acids of all degrees of strength, from actual mineral acids to phenolic bodies exerting a feeble acid function, and the solution which may appear perfectly neutral to one indicator, such as methyl orange or congo red, may be strongly acid to another such as phenolphthalein. The question is further complicated by the fact that

the tannins themselves seem to possess feeble acidity, and that means such as gelatin, hide-powder, or animal charcoal used to remove them generally absorb or destroy also a portion of the other acids present. As a rule, any of the methods described below will give results of approximate accuracy if applied to determine a known quantity of one of the stronger acids added to a distinctly acid liquor of which the acidity has been previously determined, but naturally the presence of lime in combination with phenolic bodies may render determination abortive, and in any case no two methods can be compared if they employ different indicators and consequently estimate different acids.*

Determination of Total Free Acids (Procter).—Measure 10 c.c. of perfectly clear liquor into a beaker, and add clear saturated lime water from a burette till a trace of permanent cloudiness is produced. Repeat several times, and take the average. The beginning of turbidity is best seen by looking through the liquid at printed paper. For most tannery purposes it is sufficient to merely note the c.c. of saturated lime water consumed for 10 c.c. of liquor, but it may be standardised against 10 c.c. of decinormal HCl, with phenolphthalein or methyl orange, and the acidity of the liquors calculated as equal to — grm. acetic or lactic acid per liter; N/10 acid being equal to 6 grm. acetic and 9 grm. lactic acid. If oxalic or free sulphuric acid is present, turbidity may be produced on the first addition of lime water. In this case, add excess of neutral calcium chloride to the liquor, make up to double its original volume, filter, and use 20 c.c. instead of 10 c.c. Pine-bark liquors are said to produce a similar turbidity, which may perhaps be removed in the same way. Half the free carbonic acid is estimated by this method, but may be removed previously by adding salt, and shaking; the liquor must in this case be made up to a definite volume before titrating. (Simand.) Gallic acid behaves approximately as a monobasic acid.

Determination of Free Acids, Koch's Method† as improved by Paessler and Spanjer.‡—This method depends on the removal of tannin by precipitation with gelatin, of which a solution, 2 grm. per liter, is used. 25 c.c. of the filtered liquor is mixed

* Cp. Bennett and Wilkinson, *Journ. Soc. Chem. Ind.*, 1907, p. 1186.

† *Dingl. Polyt. Journ.*, 1887, cclxiv. p. 395.

‡ *Deutsche Gerber-Zeitung*, 1899, lxxvi., lxxvii.; 1900, xlv., l. to liii., lv., cliii. to clvi.; *Collegium*, 1903, pp. 10, 17.

with 25 c.c. of the gelatin solution[†] or in liquors containing much tannin with a larger quantity, or a somewhat stronger gelatin solution may be used. After thoroughly mixing, the unfiltered liquid is titrated with N/10 sodium hydrate solution, or with baryta or lime water which has been standardised against acetic acid, withdrawing after each addition a small drop on a glass rod and spotting it upon azolitmin paper. The end of the reaction is when a blue edge appears round the spot. Should this point have been passed the titration is repeated. The acidity is calculated in terms of acetic acid per 100 c.c. or per liter of the original liquor. As some gelatins have an acid reaction, it is desirable to do a blank with the gelatin solution employed, and to deduct from the amount of lime or baryta water used the quantity which is required for the gelatin alone. All acids which are capable of reddening azolitmin paper are estimated by this method, except the tannins which combine with the gelatin. Carbonic acid is almost without effect if the end reaction is taken when the paper ceases to be brightly reddened, but will be included if the titration is taken to a full blue. The authors quote experiments made with known added quantities of acetic and lactic acids in which the results do not vary from the truth by more than a few milligrams of acid per 100 c.c. Most if not all acids which redden azolitmin will swell hide, and consequently, the method may be taken as a measure of the swelling acids present, though their actual swelling power is sometimes destroyed by the presence of salts or putrid ferments. Procter's method, on the other hand, gives all those acids which will dissolve lime, and consequently includes weak acids which have soluble lime-salts, but practically no swelling power. The choice between the two methods, therefore, depends on the object of the determination.

Determination of Total Free Acids (Kohnstein and Simand)

This method is laborious and of doubtful accuracy. 100 c.c. of the liquor is heated to boiling with 3 to 4 grm. of pure freshly ignited magnesia free from lime. The liquid is filtered, and in the clear and almost colourless filtrate the magnesia is estimated gravimetrically (after removing lime, if present, with ammonium oxalate). The total acid in terms of acetic acid is calculated from the magnesia so found, by multiplying its weight by 3 ;

* Dingl. Polyt. Journ., 1885, cclvi. pp. 38, 84.

($\text{MgO} = 40$, $2\text{C}_2\text{H}_3\text{O}_2 = 120$). Sulphuric acid may also be estimated by evaporating a portion of the filtered magnesia solution to dryness, igniting, moistening with carbonic acid water, drying, and washing on a filter, when any magnesium sulphate will pass through, while magnesium carbonate or oxide corresponding to the organic acids will remain on the filter. If the liquors naturally contain magnesium salts, these must be previously determined and allowed for in calculating the acids. (Cp. p. 45.) The method obviously estimates all acids which form soluble magnesia salts, and the salts of such acids which are decomposed by magnesia. Probable sources of error are the instability of the magnesium tannates, and the tendency to form basic salts.

Simand* also gives the following method. 50 c.c. of the liquor, which must not exceed 1.004 – 1.005 S.G. (4 – 5° Bkr.), is boiled for five minutes with return-flow condenser with 5 grm. of pure freshly ignited animal charcoal, which has been freed from mineral constituents by digestion with acid and washing. After cooling, the condenser and flask are rinsed out on to a filter, and the animal charcoal washed with boiling water till the filtrate amounts to nearly 500 c.c., and after heating on the water bath to drive off carbonic acid, and cooling, is made up to exactly 500 c.c. Of this liquid, 200 c.c. is titrated with $\text{N}/10$ sodium hydrate, or lime water and phenolphthalein. Minute traces of acid are retained by the charcoal, and for very exact analyses this must be determined by treatment of a known acid solution in a similar manner and allowed for, but the amount is so small that it may generally be neglected. This method has been adopted by the American Leather Chemists' Association, who dilute liquors $1:5$ and use 2 grm. animal charcoal to 100 c.c., titrating an aliquot part; but it has not proved very satisfactory. Hoppenstedt† has suggested a method in which the tannin is precipitated by alcoholic solution of quinine, for which he claims good results, which have not been wholly confirmed.

The determination of free acid is of great practical importance, especially in sole-leather tanning, where a deficiency invariably leads to discoloration, which is sometimes not noticeable till the leather is dried.

* Böckmann's *Chemisch-Technische Untersuchungsmethoden*, 552.

† *Journ. Am. L. C. A.*, 1906, pp. 192, 221.

Carbonic acid only exists in liquors in which fermentation of carbohydrates is going on, and is not found in putrid liquors. It is also present in drenches. It may be determined by boiling 100 c.c. of the fresh unfiltered liquor in a flask connected with a U-tube or other absorption apparatus containing an ammoniacal solution of barium chloride, which is afterwards rapidly filtered with as little exposure to the air as possible, washed with boiling distilled water, dried at 105°C ., and weighed. Simand found an average of about 0.15 grm. per 100 c.c. in sole-leather colouring liquors.

Volatile Acids (Acetic, etc.).—These may be determined by distilling 100 c.c. of the liquor in a tubulated retort with a good condenser to small volume, say 25 c.c., titrating the distillate with lime water or N/10 caustic soda and phenolphthalein, adding 100 c.c. distilled water to the retort, and repeating the operation so long as any material quantity of acid comes over. The quantity so found may be deducted from the total, and the remainder calculated into lactic acid (2 of acetic equal 3 of lactic acid). In sumach, myrobalan, or divi-divi liquors, the fixed acid is mainly gallic, of which N/10 soda is equal to about 17 grm. per liter when phenolphthalein is used, but the end-point is very uncertain. If it be desired to determine the volatile acids present in combination with bases, slight excess of phosphoric acid (free from volatile acids)* may be added to the residue in the retort, and the distillation repeated. The separation from lactic acid is not quite exact, some lactic acid being carried over.

Microscopic Examination.—The liquor is allowed to settle—best in a conical glass—and the sediment, as well as any scum is examined under a thin cover-glass, first with a low, and then with the highest power at command, and the forms and sizes of bacteria and ferments noted. Occasionally crystals (needles) of catechin may be noted if gambier is largely used. For more complete bacteriological examination, cp. Section XXVI.

Viscous Fermentation, probably due to various bacillus ferments, produces a "ropy" or treacly condition of liquor, from the formation of gummy matter, which may be separated and estimated by the method given for dextrin in the examination of leather. Valonia liquors are most liable to this disease.

(Cp. p. 435). It must not be forgotten that lime salts of tannins are also precipitated by strong alcohol.

Valuation of Liquors.—The chemist is often called upon to make an estimate of the value of liquors in a tannery, but so many circumstances are involved that at most a somewhat rough approximation can be given. It is generally out of the question to analyse each liquor individually, and it is sufficient to determine the amount of "tanning matter" per barkometer degree in a few different stages of the process, and calculate the value of the other liquors from their barkometer strength. It will be found that the tanning strength diminishes much more rapidly than the barkometer degree as the liquors become weaker, because only the tanning matter is absorbed by the skin, while the non-tannins accumulate. The proportion of the two may be approximately estimated from the hide-powder analysis. The different tanning value of liquors in different parts of the yard will be best adjusted by deducting a fixed number of barkometer degrees in each case before estimating value. Thus if a layer liquor of 50° barkometer contains 4 per cent. of tanning matter, and a handler liquor of 20° only 1 per cent., we may deduct 10° throughout, and say that each degree above 10° is equal to 0.1 per cent. of tannin. If the analysis and value of the materials are known, it is easy to determine the cost value of 1 per cent. of tanning matter; remembering that carriage, and with solid materials cost of grinding, must be added to the original price, and that the tanning value of materials shown by analysis must be diminished by an allowance for loss in leaching.

If the actual cost or value of the materials is not known, average strengths and market values must be taken. The weight of the liquors may be conveniently taken at 10 lb. per gallon, or 62.25 lb. per cube foot, and this will be strictly accurate if the liquors are measured instead of weighed for analysis.

Pits containing hides and dusting materials do not usually contain more liquor than two-thirds of their total capacity. Value of dust may generally be included with that of the liquor. For stock-taking purposes the value of all material in the leaches may be taken at half-cost, but this is generally an over-estimate.

The Valuation of Tannage of leather in process of manufacture is very difficult, but for stock-taking it is convenient to estimate it in terms of the liquor which has been used in the

process. Thus, if the liquors in a handler shift fall from 3 per cent. to 1 per cent. of tanning matter, and one fresh liquor is given for each pack of goods, the pack will gain the value of one liquor of 2 per cent. in passing through the shift. Where dust is used its value must be added. For most stock-taking purposes it is sufficient, in a systematically worked yard, to estimate such a value once for all for each stage of the process, and adhere to it so long as the method of work is unaltered. The difference of cost of tanning materials from year to year is, of course, taken into account in costing the liquor as already described. Labour should be separately allowed for. Unless the value of tannage during manufacture is properly taken into account, any attempt at costing by setting annual expenses against production is illusory, except over a long average of years. The degree of tannage actually attained can of course be accurately determined by Kjeldahling. For the complete analysis of leather see Section XXII.

Spent Tanning Materials must generally be dried and ground and extracted like other solid materials, somewhat large quantities being used, and the weak liquors concentrated by boiling. For a series of determinations it is often convenient to use the Löwenthal method, which gives good comparative results. In this case concentration is unnecessary.

It is generally most convenient to calculate the percentage on the dry substance, but in comparing the results with the original material, the loss of weight in leaching and drying must not be overlooked. If the composition of the unleached material is known, the original weight of the leached sample may be calculated from the insoluble matter present. Thus, if the original material contained 45 per cent. of insoluble matter, and the spent material 83 per cent., the tannin found in the latter would be multiplied by $\frac{45}{83}$, to reduce it to that of an equal original weight. This correction is of the greater importance the stronger the material. Where the actual analysis of the original material is unknown, the correction must be calculated from that of an average sample.

SECTION XVII.

*ANALYSIS OF THE MATERIALS USED IN
ALUM AND CHROME TANNAGES.*

Alum Tannages.—In these the principal materials employed are salt, with ammonia or potash alum, in conjunction with which flour and egg-yolk are frequently used as fillings. Recently, sulphate of alumina has largely superseded alum, of which it is the only useful constituent, since improved materials and process of manufacture have enabled its production in a practically pure state, and free from iron. In the manufacture of those leathers where colour is of secondary importance, less pure forms (such as "aluminoferric") containing traces of iron are equally suitable, if there is any material advantage in price. The value of these materials is principally dependent on the amount of alumina present, and on the absence of iron as an impurity. It is also sometimes necessary to determine the acidity, but this is usually of minor importance, except in the examination of used liquors for the study of the tawing process. Alumina is Al_2O_3 , and all the salts follow the same type, the chloride being AlCl_3 (or Al_2Cl_6), the sulphate $\text{Al}_2(\text{SO}_4)_3$, and so on. In addition to normal salts, alumina is very prone to form "basic" salts, which may be viewed as compounds of the normal salts with additional quantities of aluminium hydrate. The "basic chlorides" are thus really oxychlorides, of which several exist. Such basic salts are formed by dissolving freshly precipitated alumina in solutions of the normal salts, or by neutralising a portion of their acid with an alkali. The greater the basicity, the less stable is the compound formed: thus the more basic salts are readily precipitated by boiling, or in some cases, even by diluting their solutions. This instability renders them more easily taken from solutions by the hide fibre than the normal salts, and hence their use in tanning, and in mordanting fabrics. It is in many cases uncertain whether the basic salt is absorbed by the fibre as a whole, or whether the base and the acid are fixed by the carboxylic and amido groups, independently, leaving a more or less basic salt in solution, or whether

the process is not one of adsorption, rather than chemical combination. What has been said in this respect of alumina salts is also applicable to those of iron and chromium.

Determination of Alumina.—In most cases where other bases are present, gravimetric methods are most satisfactory. To the nearly boiling, and somewhat dilute solution, ammonium chloride is added to prevent possible precipitation of traces of lime, and then ammonia in very slight excess, and the boiling is continued till the free ammonia is almost completely expelled. The operation is best performed in a platinum or porcelain basin, as glass is apt to be somewhat attacked by the hot ammoniacal solution. The precipitate should be washed several times by decantation, and then thoroughly on the filter with boiling water (p. 12). For accurate work, after removing most of the residual solution, the precipitate should be redissolved off the filter with dilute hydrochloric acid, and reprecipitated as before and returned to the same filter, thus removing traces of co-precipitated bases. If the analysis is to extend to these, the washings and filtrate from the second precipitation should be united with those from the first. If a suction or vacuum filter is available, its use is convenient, as the precipitate is bulky and gelatinous, and is so far freed from water by suction that the still damp precipitate may be ignited with care without further drying. If the vacuum filter is not used, the precipitate must be thoroughly dried, and transferred with its paper to a platinum or porcelain crucible, where it must be ignited at first very cautiously with the cover on to avoid loss by splintering, and then very strongly over the blowpipe. If the alumina salt has been a sulphate, this strong ignition must be continued for five or ten minutes, to drive off the last traces of sulphuric acid. As the precipitate is difficult to wash, small quantities of substance (0.5–1.0 gm.) only should be used.

If iron is present, it is best to precipitate it as Fe_2O_3 along with the alumina, and afterwards to estimate its amount either in a separate portion of the solution, or after dissolving the very insoluble ignited precipitate by digestion with sulphuric acid as described on p. 364. For very small quantities the colorimetric method (p. 40) is most satisfactory, while larger amounts are determined volumetrically.

A very accurate and convenient method of estimating small

quantities of iron in the ferric state, unaffected by the presence of salts of aluminium or chromium, is that of employing it to liberate iodine from a solution of potassium iodide, and titrating the iodine with sodium thiosulphate and starch. The iron must be wholly in the ferric state, but may be sulphate or chloride, and the solution must not contain free chlorine, bromine, or nitric or chromic acids. If the iron oxide has been dissolved in concentrated hydrochloric acid after ignition, the liquid must be diluted and well boiled to expel any chlorine evolved. If the iron is not wholly ferric it may be oxidised by the addition of bromine-water, and subsequently boiled to expel all free bromine. A portion of the solution, preferably about 10 c.c. and containing as nearly as possible 0.1 gm. of Fe is placed in a bottle with a well-fitting stopper, and 30 c.c. of a 10 per cent. solution of potassium iodide is added. It is generally directed that the bottle should be heated to 50°–60° C. for 15–20 minutes, in which case the stopper must be securely tied or wired in, but in the author's laboratory no increased result was obtained by heating over that got by allowing the mixture to stand for half an hour at laboratory temperature. The contents of the bottle are now rinsed into a beaker with distilled water and titrated with N/10 thiosulphate solution in the ordinary way (cp. pp. 258 and 306). Each c.c. of N/10 thiosulphate corresponds to 0.0056 gm. of Fe or 0.008 gm. Fe_2O_3 , or the thiosulphate may be standardised directly against ferric solution of known strength. As hydrochloric acid frequently contains traces of chlorine, and potassium iodide or iodate, both of which liberate iodine, a blank determination should be made, and the thiosulphate used (if any) deducted before calculating the iron. According to Fresenius the iron solution should be nearly neutral, but in the writer's experience the result is more accurate if it is freely acid. If neutral, therefore, 20 c.c. of N/1 HCl may be added to the mixture, and even large excess produces no ill effect.

A method more suitable for larger quantities and especially when the iron is mainly in ferrous state, is that of titration with permanganate after reduction by zinc to the ferrous state. For this purpose a measured quantity of the solution, which should not contain more than about 0.1 or 0.2 gm. of iron, is transferred to a flask, strongly acidified with pure sulphuric acid, and the neck of the flask is closed with a cork through which passes

a short tube drawn to a capillary opening to permit the escape of the hydrogen evolved, or preferably with two tubes, through one of which a slow current of carbon dioxide (or coal-gas) is passed into the flask to expel oxygen. The solution is warmed, and then fragments of zinc (free from iron*) are dropped in, together with a small piece of platinum foil or a few drops of platinic chloride to set up electrolytic action, until the solution becomes colourless, and a small drop withdrawn on the end of a glass rod produces no redness with potassium thiocyanate solution. In place of zinc, coarsely powdered magnesium may be used. The heating is continued till the zinc is entirely dissolved, and the solution is titrated with N/10 potassium permanganate solution (3.16 gm. per liter), till a faint pink coloration is produced. Each c.c. of permanganate corresponds to 0.0056 gm. of Fe, or 0.008 of Fe_2O_3 . Dilute permanganate solution does not keep well, but a N/1 solution remains unchanged for a considerable time, and may be diluted as required. Permanganate solutions must always be used with a glass-tapped burette. If the strength of the permanganate is unknown, a check experiment is made by dissolving about 0.1 gm. of the fine soft wire used for binding flowers (after polishing off any oxide with emery cloth) in 10 c.c. of dilute sulphuric acid (1 : 10) with the same precautions as in reducing by zinc. As the permanganate consumed is to the weight of iron, so will be that used for the unknown solution to the iron there present. In place of iron wire, pure ammonio-ferrous sulphate, $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ may be powdered and dried between blotting paper, and dissolved in dilute sulphuric acid. 0.7 gm. of this salt contains 0.1 gm. Fe. Nitric acid, if present in the original solution, must be expelled by prolonged boiling during reduction. In presence of hydrochloric acid or chlorides, the cold solution must be diluted after reduction with 300 or 400 c.c. of boiled distilled water, which has been allowed to cool in a closed flask, and freely acidified with sulphuric acid and 3 or 4 gm. of manganese sulphate or magnesia sulphate must be added before titrating, but the results are less reliable than where sulphuric acid only is present.

Gravimetric methods of separating iron from alumina are

* It zinc quite free from iron cannot be obtained, a weighed quantity must be used in which the iron has been determined in a blank experiment and allowed for.

given on p. 264, but the volumetric methods are generally more rapid and accurate. Iron is easily separated from chromium by fusing the mixture with sodium carbonate and adding ammonia, Fe_2O_3 is precipitated and sodium chromate remains dissolved (*loc. cit.*).

Estimation of Acids.—Total sulphuric acid may be determined in the usual way with barium chloride as described on p. 46, or by the benzidine sulphate method (p. 47). Hydrochloric acid is titrated with argentic nitrate in presence of neutral potassic chromate and sodium acetate, or after neutralising with magnesia or calcium carbonate (p. 40). The free acid in solutions of aluminium sulphate or chloride may be approximately determined by titrating solutions of about decinormal strength with N/10 sodium hydrate in presence of methyl orange, but to many people the change of colour is difficult to observe, as the indicator is affected by the acid reaction of the neutral salt. The recognition of the end point is assisted by comparison with a similar quantity of water with the same amount of indicator, of which the colour is fully turned by a drop or so of N/10 acid.

A more accurate method is that of Beilstein and Grosset (quoted by Sutton), which depends on the insolubility of alum and other sulphates in absolute alcohol. 1–2 grm. of the sample is dissolved in 5 c.c. of water, 5 c.c. of saturated neutral solution of ammonium sulphate is added, and the mixture is stirred for 15 minutes. 50 c.c. of absolute alcohol is now added, and after a short digestion, the mixture is filtered through a small filter, and washed with 50 c.c. more of absolute alcohol. The solution is distilled to recover most of the alcohol, and after evaporation on the water-bath to drive off the remainder, is titrated with N/10 sodic hydrate or carbonate, and methyl orange. If preferred, the alcoholic solution may be titrated without evaporation, using caustic soda or lime water and phenolphthalein. Commercial sulphate of alumina frequently contains considerable traces of free acid. These are of little consequence for most purposes in leather manufacture, and may be easily neutralised by the addition of a little soda, which merely forms soda alum, or if in excess, makes the solution slightly basic. The use of basic solutions for tanning was patented some years ago by Mr. Bertram Hunt,* and they have some advantages

* Eng. Pat. 15,607, 1884, now expired.

over those of normal salts. The amount of basicity may of course be found by determining the relative quantities of alumina and acid.

Crystallised alums are generally practically neutral, while sulphate of alumina is sometimes acid, and sometimes basic, but in the latter case, the alumina is probably fully as available for tanning as in the normal salt.

The total acidity of solutions of chlorides or sulphates of aluminium may be determined with very approximate accuracy on the principle of *Hehner's method* for "permanent hardness," though a portion of the acid is obstinately retained by the precipitate (p. 32). In the case of sulphate of alumina, 5 grm. of the sample is dissolved in about 40 c.c. of water, and 50 c.c. of N/1 sodium carbonate is added, and the mixture boiled for a short time. The liquid is then made up to 100 c.c., filtered, and 20 c.c., representing 1 grm. of the sample, and 10 c.c. sodium carbonate solution, is repeatedly titrated with N/1 sulphuric or hydrochloric acid and methyl orange. Deducting the acid used from 10 c.c., each c.c. of deficiency represents 0.049 grm. of H_2SO_4 , 0.0355 of Cl, and in absence of other bases precipitated with sodium carbonate, 0.009 of Al. The method is not applicable to ammonia alum, or in presence of ammonia salts, on account of the volatility of the liberated ammonium carbonate, though possibly by using N/10 solutions, and digesting for some time in the cold in a stoppered flask instead of boiling, correct results might be obtained. If the original substance contains free acid, this must be determined and deducted before calculating alumina. The writer, after repeated attempts, has failed in obtaining satisfactory results either from *Bayer's method*, or its modification quoted in *Sutton's 'Volumetric Analysis.'* * (Cp. also p. 265.)

The atomic weight of Al is 27, and of Al_2O_3 102. Potash alum, $\text{Al}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4 \cdot 24\text{Aq} = 948$; ammonia alum, $\text{Al}(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 24\text{Aq} = 906$. Crystallised aluminium sulphate is $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{Aq} = 666$. As Al_2 is hexavalent in these salts, one-sixth of their atomic weights per liter produce normal solutions.

Chromium Compounds used in Tanning.—Chromium (Cr = 52) forms four oxides. The lowest, chromous oxide, CrO , corresponds to ferrous oxide, and forms analogous salts, which absorb oxygen with such rapidity that they can only be pre-

served, with difficulty. Blue solutions of chromous salts may be obtained by treating acid solutions of chromic salts with excess of zinc or electrolytically by reduction with nascent hydrogen at the cathode. Their use for tanning has been patented by Berthoin.* Such solutions might be used to reduce chromic acid in the two-bath process.

The second oxide, chromic oxide, Cr_2O_3 (molecular weight 152), is extremely similar to alumina in its general properties. It forms a hydrate $\text{Cr}_2(\text{OH})_4 \cdot 6\text{H}_2\text{O}$, which, like alumina, has weak acid properties in presence of strong bases, and hence is soluble in potassic or sodic hydrate solution to a deep green liquid, from which, however, it is precipitated again on boiling. In ammonia it is slightly soluble, forming a pink compound, which also is decomposed on boiling. With acids it forms salts analogous to those of alumina and ferric oxide, which are often violet when crystallised (as chrome alum, $\text{K}_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot 24\text{Aq}$, mol. wt. 998), and usually form violet solutions, which become green on boiling, probably from dissociation and the formation of a basic salt.† It easily forms basic salts, which have powerful tanning properties, and are usually deep green or greenish-blue in solution. The more basic forms are very unstable, and are precipitated on boiling. The precipitated hydrate parts with water on boiling, and becomes much less soluble, both in alkalies and acids, and when ignited is converted into the oxide, which is practically insoluble in all reagents, unless it is first converted into chromic acid by oxidations at a high temperature with alkalies.

The third oxide, CrO_3 , "chromic acid," or more strictly chromic anhydride (molecular wt. 100), forms ruby-red crystals, which dissolve in water to an orange solution of chromic acid, CrO_4H_2 , similar in constitution to sulphuric acid like which it forms two series of salts, neutral chromates, mostly of a lemon-yellow colour, and acid chromates, which are orange in solution. On crystallisation these solutions yield anhydrochromates, such

as potassium bichromate, of which the formula is $\begin{Bmatrix} \text{CrO}_3\text{K} \\ \text{O} \\ \text{CrO}_3\text{K} \end{Bmatrix}$, or

* Fr. pat. 353,418, April 17, 1905.

† Some crystallised normal salts are bright green, and the nature of the change of colour is by no means certain. Probably chromium salts are much more complex than the formulæ suggest. Chromium sulphates, for instance, often contain SO_4 in a form which is not precipitated by barium chloride till the complex acid is decomposed, e.g. by boiling with an alkali.

$\text{Cr}_2\text{K}_2\text{O}_7$ (molecular weight 294), and which contains no water. The ammonium and sodium salts are analogous, but the latter crystallises with 2Aq, and is very deliquescent. Its molecular weight is 299, and hence it may usually be substituted for an equal quantity of potassium bichromate than which it is cheaper. Two parts by weight of bichromate yield approximately one part of chrome oxide Cr_2O_3 .

Free chromic acid is reduced to chromic oxide by most reducing agents, such as sulphurous, thiosulphuric and hydrosulphuric acids, by ferrous salts, and by organic compounds such as alcohol, glucose and starch. If free chromic acid alone is present, or the reducing substance is insufficient in quantity for complete reduction, so-called "chromic chromate," or "chromium dioxide" (probably $\text{CrO}_3\text{Cr}_2\text{O}_3$), is formed, and the resulting product is brown, while in presence of excess of stronger acids, green or, in some cases, violet salts of chromic oxide are produced. If the acid present is not sufficient to produce the normal salt, basic salts are formed which vary according to the amount of acid present. These salts have the property of producing completely insoluble chrome leather, unaltered even on boiling; but when certain organic substances are used for reduction, violet organic compounds are formed which are unsuitable for tanning, and act upon skin as if strongly acid. The most favourable compound for tanning contains approximately 3Cl to 2Cr, the formation of which requires 5 molecules of HCl to 1 of potassium bichromate, and is easily made by adding the calculated quantity of acid to a solution of bichromate, warming slightly, and adding glucose or sugar till the solution becomes a clear greenish-blue, carbonic acid being at the same time copiously evolved.* An equivalent quantity of sulphuric acid also produces a similar solution of similar tanning properties, but giving a somewhat plumper and firmer leather. Basic solutions are also readily prepared by dissolving freshly precipitated chromic hydrate in solutions of sulphate or chloride of chromium, or by partially neutralising the acid of the normal salts with soda or sodium carbonate.† The degree of basicity most advantageous

* Small quantities of organic matter often prevent precipitation of Cr_2O_3 . Organic acids and aldehydes are among the organic products produced, and it is probably to the former that the injurious effects are due, while the action of aldehydes is advantageous to rapid tannage. The subject has not, however, been fully investigated.

† Cp. Eng. Pats. 15,607, 1884, and 5491, 1886.

varies with the character of tannage required. The more acid solutions penetrate rapidly, but tan lightly, very basic salts precipitate in use, leaving a more acid solution.

A formula given by the author,* which has been largely employed in practical tanning, with excellent results, is 5 parts of concentrated sulphuric acid, 6 parts of bichromate (either of potash or soda), and 7 parts of good brown glucose or cane sugar. The bichromate is placed in a vessel, preferably stoneware or lead-lined, with say 12 parts of water, and the sulphuric acid gradually added with stirring so as to dissolve the bichromate by the heat produced. The glucose is now added in small portions to the hot liquor, which, if the quantity is large, may require time to cool, as the reaction is violent, and much gas and heat are evolved, while if the quantity is small, external heat (steaming) may be required to carry the reaction to its end, which is attained when the liquid is a bright green. Such a solution will contain about 10 per cent. of Cr_2O_3 , and may be diluted as required for use. The quantity of glucose is excessive, though it possibly tends to fuller leather, but about three parts is all which is actually oxidised. Certain samples of glucose, probably containing dextrine, produce the dull violet compounds referred to, and must be avoided. Excessive heat should be avoided, as it drives off the aldehydes formed, to which the rapid tanning properties of the solution are partly due.

Potassium Bichromate ($\text{Cr}_2\text{K}_2\text{O}_7$, molecular weight 294) is the usual starting-point in the formation of chromium compounds. The most important determination is generally that of the chromic acid present, on which its value depends.

* *Estimation of Chromic Acid* gravimetrically may be accomplished by precipitation as lead or barium chromate, but most satisfactorily by reducing it to chromic oxide, by boiling its solution, acidified with hydrochloric or sulphuric acid, with a small excess of alcohol, till it becomes of a clear green colour, and then, after boiling off the excess of alcohol, precipitating with ammonia, igniting and weighing in precisely the same way as alumina (p. 250). Iron, alumina or chromic oxide, if present in the original solution, may be removed by precipitation with ammonia before reducing the chromic acid. (On the separation of these metals, cp. pp. 250, 365.)

Volumetrically there are several rapid and accurate methods of estimation. A simple one, where but few analyses are to be performed, is to weigh out from a weighing bottle a small quantity of pure, dry ammonium-ferrous sulphate into a porcelain basin, add 5 or 10 c.c. of dilute sulphuric acid, and then run in the chromate solution to be tested from a burette, till a small drop withdrawn with a glass rod no longer gives any greenish shade when mixed on a white plate with a drop of freshly prepared solution of potassium ferricyanide ("red prussiate of potash"). 0.392 gm. of ammonium-ferrous sulphate contains 0.56, or $\frac{1}{2}$ of its weight of iron, and consequently corresponds to 0.052 of Cr, or 3.100 of CrO_3 , from which the quantity of chromic acid may easily be calculated.

A convenient modification of this method is to add to the weighed quantity of ammonium-ferrous sulphate a measured quantity of the chromic solution insufficient to wholly oxidise it, and to titrate back the excess of ferrous salt with standard permanganate solution. 3.92 gm. of the iron salt are just sufficient for 1 gm. of CrO_3 , and correspond to 10 c.c. of N/1 permanganate. Hence, if 3.92 gm. are weighed out, and require 2.3 c.c. permanganate solution, the quantity of CrO_3 taken has been equal to $\left(\frac{10 - 2.3}{10}\right)$ or 0.77 gm. The permanganate solution is added till a faint permanent pink is produced.

A rapid and convenient method, where many estimations have to be made, and especially with dilute solutions such as those in use in the two-bath process of chrome tanning, is as follows: A measured quantity of the chrome solution, which should not contain more than about 0.1 gm. of potassium bichromate or its equivalent in chromic acid, is placed in a stoppered bottle of 200 or 300 c.c. capacity, and 5 c.c. of concentrated hydrochloric acid, or an equivalent quantity of a dilute solution, and 10 c.c. of 10 per cent. solution of potassium iodide is added. The bottle is closed and well shaken, and allowed to stand a few minutes at least. It is then titrated with a N/10 solution of pure sodium thiosulphate (24.8 gm. per liter) until the brown coloration of the liberated iodine has nearly disappeared, when about 1 c.c. of starch solution is added, and the titration continued till the violet-blue of the starch iodide has given place to the pale greenish tint of the chromium chloride. Each mole-

cule of CrO_3 liberates 3 atoms of I, and consequently each c.c. of N/10 thiosulphate corresponds to 0.0049 gm. of potassium bichromate or 0.0033 of chromic acid. If pure thiosulphate is not at hand, a solution of about 25 gm. per liter of the purest attainable may be 'standardised' against the iodine liberated by 20 c.c. of a solution of potassium bichromate decinormal as regards oxidising power, and containing 4.9 gm. per liter, which will correspond to 24.8 gm. per liter of sodium thiosulphate. A similar method may be used to estimate the thiosulphate in "hypo liquors," by adding the liquor to be tested from a burette to the iodine solution obtained by treating 10 c.c. of the potassium iodide solution and 5 c.c. of hydrochloric acid with 20 c.c. of N/10 bichromate, which will correspond to 0.496 gm. of pure thiosulphate. No accurate results can be obtained by titrating thiosulphate solution direct with bichromate, as the oxidation is complex, and proceeds further than that with iodine. The iodide used must be free from iodate, which may be tested by acidifying a little with hydrochloric acid, when, if iodate is present, iodine will be liberated colouring the solution brown, and giving the usual reaction with starch. The hydrochloric acid must contain no free chlorine, which may be similarly detected, and if necessary allowed for, by a blank test. Thiosulphate solutions should be kept in the dark, and do not remain unchanged for more than a few weeks (cp. p. 307).

It is frequently desirable to determine not only the total quantity of chromic acid, but the relative amounts present as free acid and bichromate, or as bichromate and neutral chromate. It is obvious that all three of these cannot exist in the same solution, but it must not be forgotten that free chromic acid can coexist with other free acids, and that by any alkalimetric process they will be estimated together. Neutral chromate reacts neutral with phenolphthalein, while bichromate and free chromic acid are acid to it. If, therefore, bichromate and neutral chromate are present, the former can be estimated by adding standard caustic potash or soda solution in presence of phenolphthalein till the latter is reddened. Every c.c. of decinormal alkali will in this case correspond to 0.0147 gm. of potassium bichromate, 0.010 of "half-bound," or 0.005 of free chromic acid (CrO_3), as the question is one of acidity, and not

of oxidising power. Hence *free* chromic acid will consume double as much soda as when present as bichromate.

If a solution contains 0.100 grm. of CrO_3 in whatever form, it will require 30 c.c. of N/10 thiosulphate to reduce the iodine it evolves. If the chromic acid is free, it will also require 20 c.c. of N/10 soda to make it neutral to phenolphthalein; while, if it is present as bichromate, only 10 c.c., and as neutral chromate no soda will be required. We may, therefore, deduce the following rule. If the N/10 soda required to neutralise is less than one-third of the N/10 thiosulphate, each c.c. of soda corresponds to 0.010 of CrO_3 as bichromate, or 0.0147 of potassium bichromate, and the remainder of the chromic acid indicated by the thiosulphate will be present as neutral chromate. If the soda is more than one-third of the thiosulphate, each c.c. in excess of one-third corresponds to 0.010 grm. of free CrO_3 , and the remainder indicated by the thiosulphate is bichromate. If the soda exceeds two-thirds of the thiosulphate, the whole of the chromic acid is free, and the excess of soda over two-thirds corresponds to some other acid. As the calculation is somewhat puzzling at first sight, some examples may be given. Suppose 10 c.c. of a chrome solution requires 15 c.c. of N/10 thiosulphate and 7 c.c. of N/10 sodium hydrate, we have

$$\left(7 - \frac{15}{3}\right) \times 0.010 = 0.02 \text{ grm. of free } \text{CrO}_3,$$

and

$$\frac{15}{3} \times 0.010 = 0.05 \text{ grm. of } \text{CrO}_3 \text{ as bichromate,}$$

or

0.0737 of potassium bichromate.

If only 4 c.c. of N/10 sodium hydrate were required, we should have 0.04 grm. of CrO_3 present as bichromate and 0.01 grm. as neutral chromate, the 15 c.c. of thiosulphate employed showing that 0.05 grm. of CrO_3 in all was present.

It is also possible to estimate the free chromic acid directly, and the following methods are taken from a paper by Mr. Carlton Heal and the author, which was published in the Journ. Soc. Chem. Ind., 1895, p. 248. The first is a modification of one published by M'Culloch,* and depends on the fact that free

* Chem. News, 1887, lv. p. 2.

chromic acid is oxidised to blue perchromic acid by hydrogen peroxide, while bichromates are unaffected. Perchromic acid corresponds to the fourth oxide of chromium already mentioned, but is so unstable that little definite is known of its constitution. It is soluble in ether, forming a deep blue solution which retains its colour for a short time. The analysis is carried out as follows. A measured volume of the solution in which the free chromic acid is to be determined is introduced into a narrow stoppered bottle, or more conveniently, into a 4 oz. stoppered separating funnel, and rendered alkaline by addition of a known volume, say 5 c.c. of N/10 sodium carbonate solution and 1-2 c.c. of "10 volume" hydrogen peroxide, and about 1 inch depth of ether are added. Great care must be taken that both these reagents are thoroughly neutral, and especially the hydrogen peroxide, which is generally supplied in slightly acid solution, and in most cases requires a few drops of soda solution to make it neutral to litmus, or the amount of sodium carbonate neutralised must be determined by a blank experiment. The solution is now titrated with N/10 HCl, shaking well after each addition, till the ether takes a faint blue tinge, visible against a white background in a good light. Deducting the amount of acid used from the volume of soda solution, the remainder is the soda consumed in converting the free chromic acid into bichromate, and each c.c. of this corresponds to 0.010 of CrO_3 . If the separating funnel is employed, the neutralised solution can be run off, retaining the ether for another titration. Dreher employs the same reaction for the colorimetric estimation of chrome and chromic acid.*

Another method invented by Mr. Carlton Heal depends on the precipitation of a basic copper chromate from copper sulphate by the least trace of neutral chromate in a boiling solution. To a measured quantity of the clear chromate solution, 2-4 drops of a 5 per cent. neutral solution of copper sulphate is added, and the liquid is titrated at boiling temperature with N/10 caustic soda. Immediately the whole of the free chromic acid is converted into bichromate, and a trace of neutral chromate begins to be produced, a very noticeable brown precipitate is formed, which serves as an indicator. In clear solutions this method is equally accurate with that just described, but its practical use for chrome tanning solutions is limited by the fact that organic

matter dissolved from the skins produces a turbidity which resists all ordinary means of filtration. The determination of free chromic acid in used chrome liquors is, however, rendered of less importance by the fact ascertained by Mr. Heal and the author, that under ordinary circumstances all free chromic acid is absorbed by the skin, and only bichromate is left, which does not seem to be taken up in appreciable quantities.*

Determination of Chromium in solutions of chrome salts, such as the basic liquors used in tanning, in the absence of organic matter, is of course easily performed gravimetrically like that of alumina by precipitation with ammonia, as has been already mentioned. Rough estimations may perhaps be made colorimetrically, but the colour of basic solutions varies so much that no great accuracy can be expected. Better results are obtained by oxidation with nitric acid, or hydrochloric acid and potassium chlorate or a persulphate, and comparison in alkaline solution as neutral chromate. Acid chromates are much influenced in colour by dilution and the presence of neutral salts. Its rapid volumetric estimation, however, is a matter somewhat difficult. The problem is to find an oxidising agent which is powerful enough to oxidise the whole of the chromium to chromic acid, and which can itself be completely removed from solution before titrating with iodide of potassium and thiosulphate. Hydrogen peroxide, which naturally suggests itself, although it raises some chromic acid to a still higher state of oxidation, acts also as a partial reducing agent, with evolution of oxygen. Sodium peroxide in alkaline solution oxidises chrome salts rapidly to chromic acid, but must be completely destroyed by boiling before acidification, which demands perhaps half an hour, and considerable care is needed to secure complete oxidation, and to avoid low results.† The following method is satisfactory in absence of organic matter, in the presence of which it is liable to fail from the formation of green alkaline manganates which are not decomposed by boiling. A measured quantity of the chrome solution, which should not contain more than 0.25 grm. of

* Cp. Journ. Soc. Chem. Ind., 1895, p. 248; 1900, p. 226.

† Alden (Journ. A.L.C.A., 1906, p. 174; Collegium, 1906, p. 327) obtained very satisfactory results with sodium peroxide, and states that a few minutes' boiling is sufficient to destroy any excess. It is undoubtedly the most convenient reagent. For oxidising by fusion, Alden recommends the use of sodium peroxide in an iron crucible.

Cr_2O_3 is rendered decidedly alkaline with sodium hydrate and raised to a boil, and N/1 potassium permanganate is added till the supernatant liquor remains pink after boiling for two or three minutes. A drop or two of alcohol is now added, and the boiling continued till the pink disappears, when the solution is cooled, made up to 250 c.c. and filtered, and the chromic acid is determined in 50 c.c. with potassium iodide and thiosulphate, as on p. 258. In most cases evaporation to dryness, and ignition with magnesia and sodium carbonate, as on p. 265, is to be preferred.

Determination of Chromium and Alumina in Leather.—General methods for the analysis of leathers and leather ashes are given in Section XXII., but as determinations of the mineral constituents of chrome leathers are frequently necessary, and form a somewhat special case, their execution may be here conveniently described.

The leather is incinerated in the usual way (p. 363), and the principal constituents of the ash are salts of alumina and chrome, frequently mixed with iron used as a dye-mordant or even as a tanning agent, and with traces of lime and alkaline salts from imperfect deliming and washing of the leather after chroming, reducing or neutralising, or from the soaps employed in fat-liquoring.

As obtained from the ignition of leather all three bases are usually in a very insoluble form, and especially chrome oxide when strongly ignited is quite unattacked even by prolonged digestion with concentrated acids. Recourse must, therefore, be had to fusion with alkaline bases with which the chromium is readily oxidised to soluble chromates, and the alumina forms soluble aluminates, while ferric oxide remains undissolved. For qualitative detection of chromium, fusion of a trace of ash in a borax bead in a loop of platinum wire is a sufficiently delicate test, minute quantities producing an intensely green glass. In absence of chromium iron produces a pale green glass in the inner or reducing, and a yellow in the outer or oxidising flame of the Bunsen burner or blowpipe, but these reactions are quite covered by mere traces of chromium. Iron may be detected by the ordinary thiocyanate or, ferrocyanide reactions in the solution obtained by digesting a portion of the ash with concentrated hydrochloric acid in a porcelain basin, the chromium remaining

mostly undissolved. Platinum should not be used, as it may be attacked by the chlorine which is liberated. There is no satisfactory qualitative test for alumina, but in absence of iron and chromium it may often be detected in the leather by moistening with an alcoholic infusion of logwood, which gives a violet coloration if alumina is present, but is useless in presence of iron and chrome, which produce still deeper colorations. For actual proof of the presence of alumina, it is necessary to resort to quantitative separation.

For this purpose it is most convenient, after powdering the ash very finely, preferably in an agate mortar, to mix it intimately with three or four times its weight of a mixture of about equal parts of dry K_2CO_3 and Na_2CO_3 and ignite it in a platinum crucible gently at first but finally before the blowpipe, placing the crucible sloping so that air obtains free access to the mixture. When the process is complete the melt should be pure yellow or at least quite free from green tinge. The operation may be shortened by the addition of small portions of sodium peroxide towards the end of the operation, but this is not only somewhat injurious to the crucible, but the peroxide must be completely decomposed by boiling before the direct volumetric estimation of the chromic acid. The Cr now exists as sodium and potassium chromates, the alumina as aluminates, and the Fe as insoluble Fe_2O_3 . The melt is cooled rapidly by placing the crucible on a cold iron plate, which makes the mass separate from the crucible, and is treated with hot water, when the Cr and Al pass into solution, and the undissolved* iron oxide may be collected on a filter, washed, ignited and weighed as Fe_2O_3 . To the filtrate (with the washings) excess of ammonium chloride is added, or the liquid is first rendered acid with HCl and boiled to expel CO_2 , and is then rendered *slightly* alkaline with ammonia and boiled to precipitate the Al_2O_3 , which is filtered off, ignited and weighed. The CrO_3 in the filtrate may now be estimated volumetrically with potassium iodide and thiosulphate (p. 258), or reduced by acidifying and boiling with a little alcohol and finally precipitated as Cr_2O_3 and estimated gravimetrically (p. 257). The same method of separation is applicable to precipitates con-

* If any considerable portion remains undissolved, it is safer to mix with a fresh portion of fusion-mixture, and repeat the fusion, so as to be sure that no Cr or Al remains undissolved.

taining Fe, Cr and Al obtained in analysis by precipitation of the "third group" metals with ammonia.

Where estimation of magnesia is not required, the fusion-mixture of potassium and sodium carbonates is conveniently replaced by one of equal parts of MgO and Na_2CO_3 , which does not fuse but merely sinters, so that it can be readily and frequently stirred with a platinum wire. If the quantity of mixture does not exceed 1 or 2 grm., the oxidation is readily completed in about 20 minutes over a Teclu burner. The mixed chromates are dissolved with dilute HCl , and the chromic acid is estimated with potassium iodide and thiosulphate as on p. 258. The same method is conveniently applied to chrome-liquors, by evaporating a measured quantity to a small bulk in the crucible, adding the fusion-mixture, and after evaporation to dryness, and, if necessary pulverisation, completing the ignition as above.

With the methods which have been given in this section, there is no difficulty in determining the proportions of chromic acid, chromate and bichromate in a used liquor containing chromates only, but the question is much complicated if normal and basic salts of chromium and aluminium must also be considered. The degree of basicity of chrome liquors is also difficult to determine, especially where aluminium is also present.

In this case the only accurate method is probably to determine the whole of the bases and the whole of the acids, but results of very considerable accuracy are obtained by titration of the diluted boiling solution with $N/1$ sodium hydrate in presence of a rather large quantity of phenolphthalein. None of the ordinary impurities contained in tanning liquors interfere.*

Kopecky† estimates acidity by boiling with magnesium carbonate, and determining magnesia in the filtrate, and from this calculating the acid. The method is somewhat tedious but appears otherwise satisfactory, though the formation of basic salts does not seem unlikely. Procter and McCandlish (*loc. cit.*) attempted to estimate acidity by titrating the carbonic acid liberated by boiling with sodium carbonate, but though theoretical results were obtained when the CO_2 was liberated with acids, no good concordance with theory could be obtained with chrome salts, presumably from the formation of undecomposed

Procter and McCandlish, Journ. Soc. Chem. Ind., 1907, p. 458.
Journ. A.L.C.A., 1906, p. 261.

basic salts. Appellius and Schall have recently published a similar method in which the CO_2 is absorbed and weighed, and the experiments they quote show a satisfactory agreement with theory.

Much chrome liquor is usually run away unexhausted, from the fear that for want of more accurate knowledge it cannot be so strengthened as to exactly reproduce its original character. This fear is usually much exaggerated, and the practical chemist finds no difficulty as a rule in using the same liquor repeatedly, but where this is not done the recovery of the chrome is worth attention. Probably the cheapest way is to reduce the whole to chrome oxide with "hypo" liquors, and after precipitation with lime, to furnace the sludge with potash or soda and recover bichromate. A more practicable method for tanners is to precipitate with sodium carbonate, and to use the chromium hydrate in the production of basic liquors. Chromic acid may be precipitated by barium hydrate, or barium chloride with an equivalent of lime or soda, and the barium chromate so obtained, acidified with sulphuric acid, will give a solution of chromic acid which may be used in the two-bath process.

SECTION XVIII.

DETECTION AND ESTIMATION OF GLUCOSE.

THE detection and estimation of sugars (glucose, etc.) is important to the leather manufacturer in several directions. In leather, glucose or starch syrup is often employed as a weighting material, and its detection and the estimation of added weight are often desired. It is sometimes similarly added as an adulterant to extracts, but bodies which behave like sugar are normally present in most tanning materials, where they play an important part as sources of acetic and lactic acid which are required in the liquors. It is obvious, that as traces of sugars are always found in tanning materials and therefore in leather, it is necessary, in order to prove adulteration, to know how much may be naturally present, and to determine quantitatively that more

exists than can be so accounted for. For some further information on sugar in tanning materials, see pp. 276, 360.

As the quantities found are often very small, it becomes desirable to somewhat vary the methods adopted in ordinary sugar determination, so as to avoid the necessity of concentration, and of the use of inconveniently large quantities of material. The subject has been investigated by Simand* and by v. Schroeder, Bartel and Schmitz-Dumont,† and the methods given are selected from those they describe. They are modifications of that originally discovered by Fehling.

Preparation of Fehling's Solution.—This is best prepared in two separate solutions which are only mixed at the time of using. It is suitable either for Fehling's original volumetric method, or for the gravimetric process of Allihn and its modification adopted by v. Schroeder.

(1) 34.639 grm. of the purest crystallised copper sulphate is dissolved in distilled water, 10 c.c. of normal sulphuric acid is added, and the whole made up to 500 c.c.

(2) 173 grm. of pure crystallised potassium sodium tartrate (Rochelle salt) and 125 grm. of caustic potash "pure by alcohol," are dissolved in water and made up to 500 c.c.

Simple Volumetric Method.—Though of less accuracy than the gravimetric method (which should always be used where an absolute determination is required), the volumetric method is sometimes very convenient as affording an approximate estimate of the sugar present, or as a semi-qualitative test for adulteration. Solutions containing tannin must be detannised and decolorised by basic lead acetate solution as described below, but where great accuracy is not expected it is not always important to remove the excess with sulphate.

The decolorised and neutralised sugar solution, which should contain about $\frac{1}{2}$ per cent. of reducing sugar, is placed in a burette. 5 c.c. of each of the solutions 1 and 2 are placed in a small flask or boiling tube held in a clip in a retort stand; 40 c.c. of water are added and a few pieces of broken pipe-stem to prevent bumping. The liquid is brought to a boil over a small flame, and the sugar solution is run in 1 or 2 c.c. at a time, the liquid being boiled up between each addition. When the blue colour

* Zeit. für angew. Chem., 1892, Heft 22.

† Ding. Polyt. Journ., ccxciii. (1894), p. 229.

has nearly disappeared, the sugar solution may be added in smaller quantities, and the red cuprous oxide allowed to subside after boiling, until on looking through it at a window, or white surface, the supernatant liquor appears colourless, or faint yellow. The requisite amount being approximately found in this way, a second titration must be made, adding nearly the whole of the required sugar solution at once, so that the entire boiling does not last longer than two minutes. Approximately 10 c.c. of a $\frac{1}{2}$ per cent. sugar solution will be required, and if less is needed, the solution should be diluted accordingly and the titration repeated. If, as is generally the case in the analysis of leather and tanning materials, the sugar solution is so weak that more than 10 c.c. is required to effect decolorisation, it is best to reduce proportionately the water otherwise added to the Fehling's solution. Considerable accuracy may be obtained by direct comparison with a standard sugar solution, diluting in both cases with water, so that the same total volume is employed, and heating in a final titration for exactly the same time.

Under the conditions given, the 10 c.c. of mixed solution will be reduced by the following approximate quantities :—

0.0500	gram. of glucose (dextrose, lævulose, or invert sugar).
0.0475	„ sucrose (cane sugar), previously inverted.
0.0678	„ lactose (milk sugar).
0.0807	„ maltose (malt sugar).

These quantities are, however, dependent on the exact conditions under which the titration is performed, and vary slightly with the dilution of the solution and the length of time for which it is boiled. It is best, therefore, to determine the amount by comparison with an actual sugar solution, and as the exact character of the sugars to be estimated is unknown, it is convenient to use sucrose (cane or beet sugar), which is always attainable in a state of great purity. Sucrose, however, is only reduced by Fehling's solution when it has been previously "inverted," or converted into glucoses, by the action of acid. These glucoses may for the present purpose be assumed to be identical in their action on the solution, though strictly this is not quite the case. A standard sugar solution may be prepared as follows : 0.95 gram. of good lump sugar is dissolved in about 75 c.c. of water, 2 c.c. of N/1 HCl is added, and the mixture is

heated in the boiling water-bath for 30 minutes. The acid is then neutralised with 2 c.c. of N/1 NaOH or Na_2CO_3 solution, and made up to 200 c.c. This solution should be equivalent to a 0.5 per cent. solution of glucose, and should decolorise a mixture of 5 c.c. of each of the two Fehling's solutions; and if this is not exactly the case, a suitable factor must be calculated for the Fehling's solution under the prescribed conditions. Unadulterated leathers rarely contain 1 per cent. and never more than 2 per cent. of sugar, except perhaps when tanned with myrobalans or pine-bark, or one or two other materials which are particularly rich in sugar, while it is hardly likely less than 5 per cent. would be added as an adulteration. Thus, if 10 gm. of the suspected leather be extracted with warm water and the solution after decolorising by addition of lead solution be made up to 250 c.c. and filtered, at least 16 c.c. will be required to decolorise the 10 c.c. mixed Fehling's solution, if the sample is not adulterated.

Von Schroeder's Gravimetric Method.—This is a modification of Allihn's method specially adapted for the small quantities of sugars naturally found in tanning materials and leathers; and is much more accurate than the volumetric method just described. As the result is to a marked extent dependent on the concentration of solutions and the time of heating, the details given must be rigidly adhered to in order to get accurate results, and the special table of Koch and Ruhsam given by v. Schroeder must be employed.*

Preparation and Decolorisation of Solutions.—It is necessary to remove all tannin and gallic acid as well as colouring matters. This is best accomplished with basic acetate of lead. The lead solution is prepared by rubbing together 300 gm. of pure lead acetate, 100 gm. of pure and finely powdered litharge, and 50 c.c. of water, and digesting the mass on the water-bath till it becomes white, water being added as required to replace evaporation. The mass is made up to 1 liter with distilled water, allowed to settle, and filtered.

10 c.c. of the lead solution is titrated with a strong solution of sodium sulphate till no further precipitate is produced, and 100 times the quantity of sulphate solution so employed is made up to 1 liter. The titration need not be very accurate, but it is better to have the sulphate a little in excess than the reverse.

Sodium sulphide may, if required, be used as an indicator by spotting on filter-paper, as on p. 56.

The tanning infusion or leather extract (see pp. 276, 360) should contain at least 1.5 grm. of solids per 100 c.c., and if the solutions employed for tannin analysis be used, it must be concentrated to this extent by evaporation. It must not, at the most, contain more than 1 per cent. of sugar, but very small quantities can be satisfactorily estimated. To 200 c.c. of this solution, which need not be carefully filtered, 20 c.c. of the basic lead solution is added, well shaken, and allowed to stand for 15 minutes and filtered through a dry filter. The filtrate should give no further precipitate with a drop of the lead solution. Should it do so, more both of this and of the sodium sulphate must be used, and allowed for in calculating the results. To 110 c.c. of the lead filtrate 10 c.c. of the sodium sulphate solution is added, and after the lead sulphate has completely settled, the liquid is again filtered through a dry filter. If the above-mentioned quantities have been used, 120 c.c. of this filtrate is equal to 100 c.c. of the original infusion, and the sugar found must therefore be multiplied by 1.2 to bring it to original value. If 30 c.c. of lead solution is required, 115 c.c. of the filtrate must be treated with 15 c.c. of sodium sulphate, and the result multiplied by 1.3.

Determination.—30 c.c. of each of the Fehling's solutions and 60 c.c. of water are put into a beaker of 200 c.c. capacity, and brought to a boil over a flame. The beaker is then placed in a boiling water-bath, 25 c.c. of the decolorised sugar solution is introduced and stirred up, and maintained at boiling temperature for exactly 30 minutes. If the sugar solution is very weak, 50 or 75 c.c. may be used, the water added to the Fehling's solution being correspondingly reduced, so that the total volume remains 145 c.c.

At the expiration of 30 minutes the liquid is allowed to settle, and at once filtered through a weighed asbestos filter by aid of the filter-pump. The filter (Fig. 18) consists of a piece of combustion tube about 10 cm. long and 1.2 cm. interior diameter. The lower end is drawn out to about half its original diameter, while a small funnel is fitted into the top with a perforated rubber cork. A small plug of glass wool is placed in the conical part to prevent fibres of asbestos being carried through, and about 3 cm. of the tube is filled with fibrous asbestos, of which

the lower part is pretty closely packed, while the upper part is quite loose. Packed in this way the filter is much less liable to choke, as a large part of the cuprous oxide is caught on the loosely packed layer. As some samples of asbestos are somewhat soluble in the solutions employed, it is well to wash the asbestos before using with hot 20 per cent. solution of caustic soda, and then with distilled water, and to make a blank experiment with a filter to ascertain that its weight remains constant.

The precipitate is thoroughly washed with hot water, and then with alcohol, and finally with a little ether to quicken the drying, which may be accomplished in an air-bath in less than 15 minutes. The tube is then gently ignited with a slight current of air through it to destroy possible traces of organic matter, and the copper reduced in a stream of pure dry hydrogen, the tube being heated by a Bunsen burner. The reduction takes place at a low temperature, and it is not necessary to bring the tube actually in contact with the flame, and especially the glass wool must not be ignited. When the precipitate has taken the colour of metallic copper, it is allowed to cool in the stream of hydrogen. A little dry air is now sucked through to expel the hydrogen, and the tube is weighed; and from the gain in weight the amount of glucose is found by means of the table on pp. 272 and 273. The same filter may be repeatedly used if the copper be removed with a few drops of strong nitric acid, and the filter well washed with water, alcohol and ether, dried and reweighed. Under this treatment a good filter should not lose any appreciable weight.

In place of using the asbestos tube and reducing to metallic Cu, small ordinary quantitative filter papers may be employed, preferably with a perforated platinum (or parchment-paper) cone in the funnel and with the aid of the vacuum-pump. As the Cu_2O is very finely divided it is sometimes necessary to use a

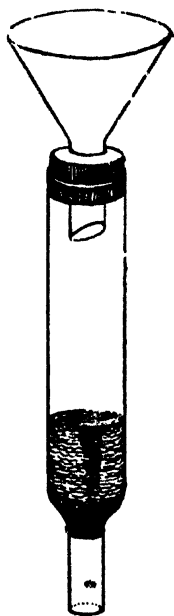


FIG. 18.

double filter. The precipitate should be first washed repeatedly by decantation to free it as far as possible from the alkaline solution, and afterwards on the filter till the latter no longer reacts with phenolphthalein. Paper absorbs and obstinately retains traces of copper, and Fehling's solution sometimes gives a slight precipitate when boiled alone, so that it is necessary to determine these errors by a blank experiment without sugar, and use the result as a correction. The paper is dried in a basin or crucible, slowly charred and heated for some time, first

TABLE FOR THE DETERMINATION OF THE GLUCOSE IN TANNING MATERIALS, FROM THE WEIGHT OF COPPER REDUCED, AFTER HEATING FEHLING'S SOLUTION WITH THE GLUCOSE SOLUTION FOR HALF AN HOUR. (*R. Koch and R. Ruhsam.*)

Cu.	Glucose.	Cu.	Glucose.	Cu.	Glucose.	Cu.	Glucose.	Cu.	Glucose.
mgr.	mgr.	mgr.	mgr.	mgr.	mgr.	mgr.	mgr.	mgr.	mgr.
1	0.4	39	16.3	77	35.1	115	54.6	153	73.5
2	0.8	40	16.7	78	35.7	116	55.1	154	74.0
3	1.2	41	17.2	79	36.2	117	55.7	155	74.5
4	1.6	42	17.6	80	36.7	118	56.2	156	75.0
5	2.0	43	18.0	81	37.2	119	56.7	157	75.5
6	2.5	44	18.4	82	37.7	120	57.2	158	76.0
7	2.9	45	18.9	83	38.2	121	57.7	159	76.5
8	3.3	46	19.3	84	38.7	122	58.2	160	77.0
9	3.7	47	19.7	85	39.2	123	58.7	161	77.5
10	4.1	48	20.2	86	39.8	124	59.2	162	78.0
11	4.5	49	20.7	87	40.3	125	59.7	163	78.5
12	4.9	50	21.3	88	40.8	126	60.2	164	79.0
13	5.3	51	21.8	89	41.3	127	60.7	165	79.5
14	5.7	52	22.3	90	41.8	128	61.2	166	80.0
15	6.1	53	22.8	91	42.3	129	61.7	167	80.5
16	6.5	54	23.3	92	42.8	130	62.2	168	81.0
17	7.0	55	23.9	93	43.3	131	62.6	169	81.4
18	7.4	56	24.4	94	43.9	132	63.1	170	81.9
19	7.8	57	24.9	95	44.4	133	63.6	171	82.4
20	8.2	58	25.4	96	44.9	134	64.1	172	82.9
21	8.6	59	25.9	97	45.4	135	64.6	173	83.4
22	9.0	60	26.4	98	45.9	136	65.1	174	83.9
23	9.4	61	26.9	99	46.4	137	65.6	175	84.4
24	9.9	62	27.4	100	46.9	138	66.1	176	84.9
25	10.3	63	28.0	101	47.5	139	66.6	177	85.4
26	10.7	64	28.5	102	48.0	140	67.1	178	85.9
27	11.1	65	29.0	103	48.5	141	67.6	179	86.4
28	11.6	66	29.5	104	49.0	142	68.1	180	86.9
29	12.0	67	30.0	105	49.5	143	68.6	181	87.4
30	12.4	68	30.5	106	50.0	144	69.1	182	87.9
31	12.9	69	31.0	107	50.5	145	69.6	183	88.4
32	13.3	70	31.6	108	51.0	146	70.1	184	88.9
33	13.7	71	32.1	109	51.6	147	70.6	185	89.4
34	14.1	72	32.6	110	52.1	148	71.1	186	89.9
35	14.6	73	33.1	111	52.6	149	71.5	187	90.4
36	15.0	74	33.6	112	53.1	150	72.0	188	90.9
37	15.4	75	34.1	113	53.6	151	72.5	189	91.3
38	15.9	76	34.6	114	54.1	152	73.0	190	91.8

DETECTION AND ESTIMATION OF GLUCOSE. 271

TABLE FOR THE DETERMINATION OF GLUCOSE—continued.

Cu.	Glucose.	Cu.	Glucose.	Cu.	Glucose.	Cu.	Glucose.	Cu.	Glucose.
mgr.	mgr.	mgr.	mgr.	mgr.	mgr.	mgr.	mgr.	mgr.	mgr.
191	92.3	249	122.1	306	152.2	363	183.7	420	216.7
192	92.8	250	122.7	307	152.8	364	184.2	421	217.3
193	93.3	251	123.2	308	153.3	365	184.8	422	217.9
194	93.8	252	123.7	309	153.9	366	185.4	423	218.4
195	94.3	253	124.2	310	154.4	367	186.0	424	219.0
196	94.8	254	124.8	311	155.0	368	186.5	425	219.6
197	95.3	255	125.3	312	155.5	369	187.1	426	220.2
198	95.8	256	125.8	313	156.0	370	187.7	427	220.8
199	96.3	257	126.3	314	156.5	371	188.3	428	221.4
200	96.8	258	126.9	315	157.1	372	188.8	429	221.9
201	97.3	259	127.5	316	157.6	373	189.4	430	222.5
202	97.8	260	128.0	317	158.1	374	190.0	431	223.1
203	98.3	261	128.5	318	158.7	375	190.6	432	223.7
204	98.8	262	129.0	319	159.2	376	191.1	433	224.4
205	99.3	263	129.5	320	159.8	377	191.7	434	225.1
206	99.8	264	130.1	321	160.3	378	192.3	435	225.8
207	100.3	265	130.6	322	160.9	379	192.8	436	226.4
208	100.8	266	131.1	323	161.4	380	193.4	437	227.1
209	101.4	267	131.6	324	162.0	381	194.0	438	227.8
210	101.9	268	132.2	325	162.5	382	194.6	439	228.5
211	102.4	269	132.7	326	163.0	383	195.2	440	229.1
212	102.9	270	133.2	327	163.6	384	195.7	441	229.8
213	103.5	271	133.7	328	164.1	385	196.3	442	230.5
214	104.0	272	134.2	329	164.7	386	196.9	443	231.2
215	104.5	273	134.7	330	165.2	387	197.5	444	231.8
216	105.0	274	135.3	331	165.8	388	198.0	445	232.5
217	105.5	275	135.8	332	166.3	389	198.6	446	233.2
218	106.0	276	136.3	333	166.9	390	199.2	447	233.9
219	106.6	277	136.8	334	167.4	391	199.8	448	234.5
220	107.1	278	137.4	335	167.9	392	200.3	449	235.2
221	107.6	279	137.9	336	168.4	393	200.9	450	235.9
222	108.1	280	138.4	337	169.0	394	201.5	451	236.6
223	108.7	281	139.0	338	169.5	395	202.1	452	237.2
224	109.2	282	139.5	339	170.1	396	202.7	453	237.9
225	109.7	283	140.0	340	170.6	397	203.3	454	238.6
226	110.2	284	140.5	341	171.2	398	203.8	455	239.3
227	110.7	285	141.1	342	171.7	399	204.4	456	239.9
228	111.2	286	141.6	343	172.2	400	205.0	457	240.6
229	111.8	287	142.1	344	172.8	401	205.6	458	241.3
230	112.3	288	142.6	345	173.3	402	206.2	459	242.0
231	112.8	289	143.2	346	173.9	403	206.8	460	242.6
232	113.3	290	143.7	347	174.5	404	207.3	461	243.3
233	113.8	291	144.2	348	175.0	405	207.9	462	244.0
234	114.4	292	144.7	349	175.6	406	208.5	463	244.7
235	114.9	293	145.3	350	176.2	407	209.1	464	245.3
236	115.4	294	145.8	351	176.8	408	209.7	465	246.0
237	115.9	295	146.3	352	177.3	409	210.3	466	246.7
238	116.4	296	146.9	353	177.9	410	210.8	467	247.4
239	117.0	297	147.4	354	178.5	411	211.4	468	248.0
240	117.5	298	147.9	355	179.1	412	212.0	469	248.7
241	118.0	299	148.4	356	179.6	413	212.6	470	249.4
242	118.5	300	149.0	357	180.2	414	213.2	471	250.1
243	119.0	301	149.5	358	180.8	415	213.8	472	250.8
244	119.5	302	150.1	359	181.4	416	214.4	473	251.4
245	120.1	303	150.6	360	181.9	417	214.9	474	252.1
246	120.6	304	151.1	361	182.5	418	215.5	475	252.8
247	121.1	305	151.7	362	183.1	419	216.1	476	253.5
248	121.6								

to a dull, and afterwards to a bright red heat, and the precipitate is weighed as CuO , which must be reduced to Cu for comparison with the table by multiplication by $\frac{63.6}{79.6}$, or practically by 0.8.

If complete oxidation is difficult, the precipitate may be moistened with concentrated nitric acid and again ignited.

Hellon, Winter Blyth, and others, redissolve the copper oxide in dilute nitric acid, and deposit electrolytically on a platinum dish, a continuous current of $\frac{1}{2}$ to 1 ampere current-density and 2.2 to 2.5 volts being used. The solution (100 c.c.) should not contain more than 3 per cent. of nitric acid, and the temperature should be 20° to 30°C . When all the Cu has been deposited, which will require from two to five hours, and may be tested by addition of ammonia to the solution, the dish is washed with distilled water while the current is still passing, till all nitric acid is removed. The deposited copper is now washed further under the tap, rinsed with methylated alcohol and then with ether, dried in water oven, cooled, and weighed, the basin being afterwards freed from copper with nitric acid. An ordinary electric supply may be used if of continuous current, the resistance being regulated by lamps. The anode is a piece of platinum foil, and the basin, forming the cathode, is connected to the negative wire, and is conveniently placed in a photographic tray to receive the washings.

It must be borne in mind that the glucoses which are employed for weighting leather are by no means chemically pure, but contain variable quantities of maltose and dextrin, the colourless glucose syrup especially containing much larger quantities of dextrin than the ordinary solid glucoses. As Fehling's solution does not reduce dextrin when free from sugar, a mere determination of glucose alone gives but little information as to the actual amount of weighting material employed. If, however, such glucoses containing dextrin are heated with dilute acid, the dextrin and maltose are converted into an equivalent weight of glucose, which can be directly estimated by Fehling's solution. Ninety-three parts of starch yield 100 parts of glucose as estimated by Fehling's solution,* and dextrin and maltose occupy an intermediate position, so that no great error is involved if it is assumed that the total

* Noyes and others, *Journ. Am. Ch. Soc.*, 1904, xxvi. 266 et seq.

weight of glucose found after conversion is equivalent to the original weight of dry matter added, since, of course, commercial glucose always contains impurities which are not converted into sugar, and it is practically impossible to hydrolyse starches and dextrans completely, the attainable maximum being of some 96 to 98 per cent. To the detannised solution containing glucose and dextrin, 10 per cent. by volume of hydrochloric acid of sp. gr. 1.125 is added,* and the solution is raised to 100° C., and heated on a water-bath for two hours, either in a closed flask or with a reflux condenser to prevent evaporation. 90 per cent. or more of the hydrochloric acid is neutralised with strong caustic soda solution, of which the necessary amount can be calculated, and the solution is made up to a known volume and either titrated against Fehling's solution as on p. 267, or determined gravimetrically as on p. 270. It is stated (*loc. cit.*) that the conversion proceeds better in solutions of 2 to 4 per cent. than in those of 1 to 2 per cent., but the time given should hydrolyse 97 to 98 per cent., even in a 1 to 2 per cent. solution. Simand† only employs 7.5 per cent. of hydrochloric acid, sp. gr. 1.125, instead of 10 per cent. as recommended above, but probably it is safer to use the larger quantity. In calculating the actual weighting of leather from the glucose found, it must be remembered that the commercial glucose is hygroscopic, and must retain at least as much (and probably more) moisture than the leather in which it is found. The average moisture of air-dried leathers is about 15 per cent., but varies with the weather. Experiment as to the actual weight given by known quantities of commercial glucoses are desirable.

The sugar naturally present in tanning materials is not merely important as influencing the calculation of weighting by glucose, but as furnishing the basis from which the natural acids of the liquors are derived by fermentation. The sugar is of more than one species, dextrose, levulose and less definitely known sorts being present in different materials, but probably the estimation as glucose by Fehling's solution gives a pretty accurate idea of their total percentage. The result of a large number of determinations by Von Schroeder‡ are given in

Loc. cit.

† Zeits. Angew. Ch., Heft 22, 1892.

‡ Gerberei-Chemie, Berlin, 1898, pp. 577-623.

the following Table. These determinations were made by the gravimetric method (p. 270) after removal of the tannin by precipitation with lead, and therefore only include the sugars existing as such ready formed in the infusion. In addition to these it is known that many tannins, like the glucoside, colouring matters, contain sugars or sugar-yielding bodies, and like these can be hydrolysed by digestion with dilute acids. The author has, however, been unable to find in literature detailed observations

SUGARS NATURALLY CONTAINED IN TANNING MATERIALS.
(Von Schroeder.)

	Tanning Matter.	Sugars.	
		Per cent. on Material.	Per cent. on Tanning Matter.
Oak bark (average 118 samples) . . .	10·5	2·7	25·2
„ inner flesh, tree 150 years old . .	13·8	1·3	9·5
„ outer crust „ „ . . .	7·6	0·7	9·2
„ young tree bark (Tharand) . . .	13·0	6·6	50·8
Oak wood. Trees over 100 years old (Mitrowitz)	7·7	0·4	5·8
„ <i>Q. sessiliflora</i> . Young oak, 19 years; wood only	2·2	1·2	53·7
Evergreen oak. <i>Q. ilex</i> , bark . . .	17·7	3·6	20·3
Garouille. Root-bark <i>Q. coccifera</i> , average	25·4	1·0	4·0
Pine bark, <i>Abies excelsa</i> , Lam., average .	11·6	3·5	33·5
Willow barks (Russian), average . . .	13·4	4·5	33·6
Mimosa barks (Australian wattles), average	28·4	0·9	3·2
Aleppo pine ("Scorza rossa"), outer bark	20·6	2·0	9·9
Henlock pine, <i>Abies canadensis</i> , old bark	12·3	7·1	5·8
Divi-divi pods, <i>Casalpinia coriaria</i> . .	40·7	8·4	20·5
Algarobilla pods, <i>C. brevifolia</i> , average .	42·9	8·2	19·1
Myrobalans fruit of <i>Terminalia chebula</i> , average	30·8	5·4	17·4
Valonia sugar very variable, average . .	28·3	2·7	9·5
Sumach (Sicilian)	27·8	4·6	16·6
Canaigre, root of <i>Rumex hymenosepalus</i> .	30·1	4·3	14·3
Chestnut wood, without bark	8·3	0·3	2·9
Quebracho wood, <i>Loxopterygium Lorenzi</i>	24·4	0·25	1·0
Cube Gambier, <i>Nauclaea gambir</i> . . .	47·2	1·9	3·9
Cutch, <i>Acacia catechu</i> , wood extract . .	39·9	0·5	1·3

either with regard to the quantities of these sugars, or the time, temperature and concentration of acid necessary for complete hydrolysis. If the heating with acid, such as is described for conversion of starch into glucose, were carried out before instead of after the detannisation with lead, any sugars liberated from the tannins would of course be estimated with those existing ready formed. The author hopes to investigate this subject further.

Von Schroeder made a number of determinations of sugars in extracts, and in many cases the results show a higher percentage than is found in the original material. It is not certain that such a result indicates adulteration with glucose, which is rarely practised, since it may be due to decomposition of tannin and liberation of glucoside sugar in the process of manufacture, the decomposition of cellulose, or the use of starchy materials in decolorising.

SECTION XIX.

ANALYSIS OF SOAPS.

SOAPS are not only of direct importance to the leather manufacturer, but their examination forms a good introduction to the study of oils and fats, and a brief account of the principal methods is therefore given. For more detailed information the reader is referred to Lewkowitsch's 'Oils, Fats and Waxes,' third edition, pp. 1074-1082.

Sampling demands considerable care, as soaps dry rapidly, and the outer part of a bar has often lost much water before it reaches the chemist. In bar soaps, it is best to use the central portion only if the original character of the soap is to be determined; and in soft soaps, the sample should be drawn from the centre of the barrel. Weighings should be made rapidly, or in closed vessels, and methods of analysis involving shaving finely before weighing are to be avoided.

Determination of Water.—About $\frac{1}{2}$ inch depth of sand, previously ignited, is placed in a beaker of about 100 c.c. capacity, together with a short glass rod, and the whole is weighed; 3 to

5 grm. soap, cut in slices, is quickly weighed to this, and 25 c.c. good alcohol added. The beaker is placed on a water-bath, and stirred till the soap is dissolved and the alcohol is evaporated, and then dried to constant weight in the air-oven at 110° C. (Gladding).*

A more rapid determination for technical purposes may be made by placing 5 grm. of the soap in a large porcelain crucible on the sand-bath, heating with a small flame, and stirring continuously with a rod weighed in with the crucible, and rough and jagged at the end to break up the lumps formed. The operation is complete when, after removing the flame, a cold glass plate placed on the crucible is no longer dewed, which should require about half an hour. Great care must be taken not to burn the soap, which is indicated by the smell. Results, if carefully done, are accurate to $\frac{1}{4}$ per cent.† In place of drying alone, a known weight of oil free from water or of known water-content may sometimes be added with advantage. Lewkowitsch points out that actual water determination is rarely important because of the uncertainty of sampling, and that it generally suffices to estimate it from the deficiency found on adding up the constituents determined by analysis. Where determination is needed, he recommends cutting the soap into fine shavings, and weighing in a porcelain dish with a glass rod with which to break up the flakes. The first part of the drying should be conducted at a low temperature insufficient to melt the soap. Soap as manufactured contains about 30 per cent. of water—if much less than this is found, the soap has been intentionally or accidentally dried; if more, water has been added, as is very frequent.

Determination of Fatty Matter and Alkali.—About 10 grm. of the soap is weighed into a 200 c.c. beaker and dissolved in about 100 c.c. of hot water on the water-bath with constant stirring. A few drops of methyl orange and 50 c.c. of N/1 HCl (or more if the acid is not in distinct excess) is gradually added, and the heating and stirring continued till the fatty matter collects in a clear oily layer on the top of the liquid. The glass rod is rinsed with hot water and the heating continued till the fats have again collected in a mass, which is

* Chem. Zeit., vii, 568.

† Watson Smith, Jour. Soc. Dyers and Colorists, i, 31.

then allowed to cool and solidify. The cake is detached from the beaker with a clean spatula, the acid liquid poured carefully into another beaker, and the cake of fat rinsed with cold water which is added to the acid solution. The fat cake is cautiously dried with filter paper and placed in a desiccator in a carefully weighed basin or clock-glass, any fat which can be scraped off the beaker being added to it; and after it has dried for some time it is weighed. If the fatty matter is not solid when cold, or in any case if it is not to be subjected to further examination, it is convenient to add 5 gm. of dry beeswax or stearic acid before cooling, and to deduct it from the weight. The beeswax is conveniently weighed in the same basin in which the fatty matter is to be weighed and added to the tare. Another rapid method susceptible of tolerable accuracy is to separate the fatty matter from the aqueous solution in a tap burette and wash it with hot distilled water. The burette is then heated in a deep beaker of boiling water, or in steam; the volume of fatty matter in c.c. multiplied by 0.85, the average specific gravity of the fatty acids at 100° C., gives its approximate weight in grams. (For more accurate methods, cp. p. 314.)

The acid aqueous solution is titrated with methyl orange and N/1 sodium hydrate or carbonate solution, the amount of which deducted from 50 c.c. gives the acid neutralised by the total alkali of the soap, which in hard soaps may be calculated as Na_2O , and in soft soaps as K_2O . If the acid solution is turbid it must be filtered before titration. An insoluble sediment at the bottom of the beaker consists of silica or "filling," such as china clay, insoluble in hydrochloric acid. Chalk or whiting is of course dissolved if present, and estimated as alkali. The "total alkali" includes that combined with the fatty acids as soap, together with any alkalies present as hydrates, carbonates, borates, or silicates. Further information on these points is obtained by repeating the analysis by the alcohol method described below. A preliminary test may be made by moistening the freshly cut surface of the soap with an alcoholic solution of phenolphthalein. A pink coloration is produced by the presence of caustic alkalies, and also, if the soap is not too dry, by carbonates, silicates and borates.

The fatty matter consists of the fatty acids of the soap, together with resin acids (p. 316) if resin has been used in the

manufacture, sometimes traces of fats which have escaped saponification (or rarely, traces of free fatty acids), and unsaponifiable matter such as petroleum products purposely added, or cholesterol and higher alcohols, derived from the use of "recovered grease," or the addition of lanolin. These can be separated to a certain extent by the methods given under oil analysis, pp. 309 *et seq.* For this purpose it will be necessary, if wax has been used, to prepare a fresh quantity of fatty matter, which need not be done quantitatively; but the liquid fats may be separated from the aqueous liquid by a tap funnel or burette, and a portion weighed out for analysis. Soluble fatty acids will dissolve to some extent in the acid liquid, from which the bulk may be recovered by saturation with common salt, but, except in the case of cocoa-nut and palm-nut oil soaps, they may generally be neglected. If a qualitative examination reveals no unsaponified or unsaponifiable matter, the fatty matter may usually be assumed to consist of fatty and resin acids. If required to add up to 100 in a complete analysis these must be calculated to fatty anhydrides, which may usually be done with sufficient accuracy by multiplying their weight by 0.965.

The alcohol method may be employed as a check on the above, and gives considerable additional information. 4 or 5 grm. of the soap, which if much watered should be somewhat dried after weighing, is dissolved in 50 c.c. of hot absolute alcohol. Any insoluble residue, consisting of mineral and organic "fillings," together with carbonates, silicates, borates, and sulphates, is filtered off on a dried and weighed filter, well washed with hot alcohol, dried at 100° C. and weighed. Organic matter may be determined in this residue by ignition, and bases existing in combination with organic acids, or as carbonates, borates or silicates, by solution in standard HCl and titrating back with soda, the indicator being methyl orange or lacmoid paper.

The alcoholic filtrate is received in a narrow-necked flask to avoid carbonation by the air; phenolphthalein is added and the solution titrated with N/1 HCl, till the red colour is discharged, and the result calculated as *caustic alkali*. After distilling off the alcohol, and free dilution with water, methyl orange is added and the titration continued to redness, the additional acid used corresponding to the alkali present as soap. It sometimes happens that no redness is produced with phenolphthalein from the

total absence of caustic alkali, and in this case free fatty acids may possibly be present. In this case the solution should be tested with a single drop of $N/10$ NaOH. If this produces no redness, the addition may be continued till redness is produced, and the results calculated as "free fatty acids," in terms of oleic.

For molecular weights of fatty acids, see p. 302.

SECTION XX.

OILS AND FATS.*

GENERAL CHEMISTRY OF OILS AND FATS.

To the chemist, oils and fats constitute a single class, merely differing in melting points and consequently in consistence—many which are solid fats in temperate climates being liquid oils in the tropics. All the true fats and oils are salts or "esters" of certain organic acids with glycerin; but the closely allied waxes, together with sperm oil and a few liquid waxes usually classed with oils, are similar esters in which members of the alcoholic series are combined with the acids, replacing the glycerin. There are also some hydrocarbons, such as paraffin wax and oil, vaseline, etc., which, though of quite different chemical character, are popularly classed with the oils and waxes; and so-called "volatile oils" of very varied constitution which are usually the odorous constituents of plants. Glycerin, as might be surmised from its solubility in water and its very sweet taste, may be viewed either as one of the simplest type of sugars, or as a trihydric alcohol, its

formula being $\begin{array}{c} \text{CH}_2(\text{OH}) \\ | \\ \text{CH}(\text{OH}) \\ | \\ \text{CH}_2(\text{OH}) \end{array}$ or $\text{C}_3\text{H}_8(\text{OH})_3$, and each of the three

hydroxyls is capable of combining with a molecule of organic acid with elimination of water, just as hydrochloric acid com-

* Cp. Lewkowitsch, 'Oils, Fats and Waxes'; and Schmitz-Dumont, *Diag. Polyt. Journ.*, 1895, ccxcvi. Heft 9-11.

binizes with sodium hydrate, $\text{HCl} + \text{NaOH} = \text{NaCl} + \text{OH}_2$. The neutral fats are therefore triglycerides, each molecule of glycerin being linked to three acid groups, which may be all similar, though there is good reason to believe that mixed esters exist, such as oleo-distearin. (The names of neutral fats are terminated in "in"—as "stearin," which is glycerin tri-stearate—to distinguish them from the free acids such as stearic acid.)

Since all the true fats are glycerides, the differences between them depend entirely on the acids; and these owe their acid nature to the CO.OH group which they contain, and their differences to the other groupings with which this is linked. All acids naturally present in fats are monobasic, or have one CO.OH group only. The acids of the ordinary hard fats belong to the series, often described as the "fatty series," of which formic and acetic acids are the simplest members. Formic acid is $\left\{ \begin{array}{l} \text{H} \\ \text{CO.OH} \end{array} \right.$; acetic $\left\{ \begin{array}{l} \text{CH}_3 \\ \text{CO.OH} \end{array} \right.$; propionic $\left\{ \begin{array}{l} \text{C}_2\text{H}_5 \\ \text{CO.OH} \end{array} \right.$; so rising by successive additions of CH_2 to palmitic acid $\left\{ \begin{array}{l} \text{C}_{16}\text{H}_{31} \\ \text{CO.OH} \end{array} \right.$ and stearic acid $\left\{ \begin{array}{l} \text{C}_{17}\text{H}_{33} \\ \text{CO.OH} \end{array} \right.$, which are the principal acids of hard tallow stearines. (The so-called "distilled stearines" from recovered greases are not true stearins, but consist mainly of their free fatty acids unaccompanied by glycerin.) In such a "homologous" series, the boiling and melting points usually rise with the increasing chain of carbon atoms, so that while formic and acetic acids are volatile liquids, the acids higher than caprylic, $\text{C}_7\text{H}_{15}\text{CO.OH}$, are solid at ordinary temperatures, and their solubility in water diminishes as their melting points increase, caprylic acid being nearly insoluble in cold water.

From the common formula of this series, $\text{H}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\dots-\overset{\text{H}}{\underset{\text{O}}{\text{C}}}-\text{OH}$

it will be observed that all the valencies or combining bonds of the atoms are employed and satisfied; and that consequently such acids are "saturated" compounds, which can only form new compounds by "substitution," and not by "addition" of new elements, and they are therefore stable substances not easily broken up.

There is, however, a second series of acids which we may call

the "oleic" series, in which the group $\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ -\text{C} = \text{C}- \end{array}$ occurs somewhere in the carbon chain, and in which the double link can be easily broken to form such compounds as $-\text{CHOH}-\text{CHOH}-$ or $-\text{CHI}-\text{CHI}-$ in place of $-\text{CH}=\text{CH}-$. Thus oleic acid is $\text{C}_{17}\text{H}_{31}\text{CO.OH}$, differing only from stearic acid by the 2H corresponding to the double link. In the laboratory, though not as yet in practical manufacture, it is easy to replace this 2H, converting oleic into stearic acid. The glycerides of acids of this series are all liquid at ordinary temperatures, and "olein" or glycerin trioleate forms a large part of most non-drying oils, and, with stearin and palmitin, of such fats as tallow and lard, which are the softer the more olein they contain.

It is obvious that more than one double link may be contained in the carbon chain, and, from linseed and fish oils, acids have been isolated containing three or even more double links. The fats of such acids are usually liquid, and absorb oxygen readily from the air, becoming converted into gummy or resinous bodies. Hence oils containing them have the property of "drying" more or less rapidly in the air, becoming converted into solid or sticky masses. Many oils, such as cotton-seed, are known as "semi-drying oils," thickening and gumming in the air from the presence of acids less saturated than oleic. The total unsaturatedness of an oil is easily determined in the laboratory, by ascertaining the quantity of iodine necessary to satisfy the unsaturated bonds; but in mixtures of acids of various series, such as constitute the natural oils, it is not usually possible to determine accurately whether the unsaturation is due to a large quantity of a slightly unsaturated acid, like oleic, or a much smaller proportion of a much more unsaturated acid, such as some of those of linseed or cod-liver oils. Some attempts in this direction are referred to in footnote, p. 331.

Fatty acids also exist in which one or more of the H atoms in the chain are replaced by OH groups, and an acid of this type of some importance is ricinoleic, the acid of castor-oil, which is hydroxyoleic acid. Ricinolein is insoluble in petroleum spirit, and most other oil solvents, but soluble in alcohol, showing in this way the effect of the hydroxyl. When unsatu-

rated oils, such as olein and the semi-drying oils, are oxidised by blowing air through the heated oil, oxygen is absorbed, and fats of oxy- and hydroxy-acids are produced in many ways resembling castor-oil, which such "blown-oils" are frequently used to adulterate. Somewhat similar reactions, but more pronounced from the greater unsaturation of the oils, take place in the manufacture of *dégras* from marine oils, in chamoising, and in the conversion of linseed-oil into linoleum-mass by oxidation.

The solid waxes, and liquid waxes such as sperm oils, consist, as has been stated, of fatty acids in the hard waxes, mostly high in the stearic acid series; as, for instance, cerotic and melissic acids from beeswax, which contain 26 and 30 atoms of carbon respectively, combined with high members of the alcohol series. Ordinary alcohols consist of a hydrocarbon chain similar to the acids, but terminated simply by the group $\text{CH}_2\text{.OH}$ instead of CO.OH . They have, therefore, no acid properties, and when treated with alkalis are unaffected, and hence appear in waxes and sperm oils as "unsaponifiables" (p. 309), but must not be confounded with the petroleum products and rosin oil which are frequently used as oil adulterants, and which are also unsaponifiable.

The structure of the petroleum products, such as benzoline, petrol, paraffin oils and waxes, may be still simpler than that of the alcohols; consisting merely of CH_2 chains, terminated at each end by CH_3 , the lightest petroleum spirit having about six carbon atoms, and the hard waxes averaging about eighteen, like the solid fatty acids. There are, however, many complications, such as branched chains (which may also occur in fatty acids and alcohols), and unsaturated compounds in which double links occur, or the two ends of the chain may be united to form a ring-compound.

The above sketch, while it may assist the less chemical reader to understand the analytical processes which are now to be described, is of course, exceedingly imperfect in detail, for which the reader is referred to larger works, and especially to that of Lewkowitsch.*

* *Oils, Fats, and Waxes* (Macmillan, 1904), 3rd edition.

A. DETERMINATION OF TOTAL FATTY MATTER, AND NON-FATS.

It is in many cases sufficient for the purposes of the leather manufacturer to determine the total amount of fatty matter present in a leather sample or elsewhere; and in others its extraction is a necessary preliminary to further examination. The most usual means of accomplishing this is by extraction with a solvent; and for general purposes the most convenient apparatus, notwithstanding its fragility, is the ordinary form of Soxhlet tube. The arrangement of apparatus will easily be understood from the figure. A is a cylindrical glass vessel which contains the material to be extracted, and which is fitted above to a vertical condenser B, so arranged that the liquefied solvent drips back on the material. A is fitted with a syphon C, which comes into action when the liquid rises high enough to cover the material, and returns it to the boiling flask D at intervals. A side tube, E, allows the vapour to pass up again to the condenser. A slender tube fitted to the top of the condenser lessens the diffusion of uncondensed vapour into the laboratory. The whole is fitted together with good corks, and it is best to deprive these of fatty matters by boiling a little of the solvent in the apparatus for some time before actually taking it into use.

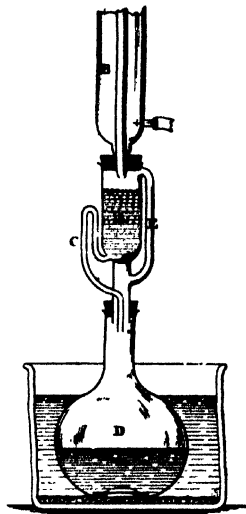


FIG. 19.

With the solvents used for oils, a hot solution of gelatin and glycerin in a little water may be applied to the joints if they cannot otherwise be made tight. The flask D is best of a spherical form, as in the writer's experience conical flasks have proved liable to fracture. It should be heated in a water-bath, preferably heated by steam or an electric resistance, and placed as far as possible from open flames and inflammable surroundings in case of accident. The flask should not come in contact with the bottom

of the water-bath, but may rest on a piece of perforated zinc or wire gauze, or be supported by a clamp.

There is considerable choice of solvents, but those most usually employed are ordinary ethyl ether, petroleum ether, and carbon disulphide; and of these the latter is generally to be preferred, as its vapours, though poisonous and unpleasant, are heavy and easily condensed, and therefore little liable to escape into the laboratory. If petroleum ether is used, it must be carefully fractionated to contain no portion boiling above 75° C., and the quantity used must not be too small, as otherwise it is very liable to cause accidents from the temperature rising in the flask much above that of the solvent in the extractor which suddenly syphons down into it. The fractionation is made easier by the addition of about 5 gm. per liter of vaseline or paraffin wax to the commercial ether before distillation (Schmitz-Dumont), and may be performed in an ordinary distillation flask with Liebig condenser, but is made much more perfect by the use of one of the various forms of dephlegmating column (see p. 11). Carbon disulphide should be kept in the dark, and occasionally distilled to purify it from dissolved sulphur.* Probably now that it is attainable at a moderate price, carbon tetrachloride is to be preferred to any of the solvents named from its non-inflammability. It boils at 78° C. and dissolves all ordinary fats, but also some substances such as lecithin which are not soluble in petroleum ether.

The material to be extracted must usually be finely divided. Leather is cut into shavings, while other substances (e.g. egg-yolk, *dégras*) are often mixed with sand or other indifferent bodies to make the mass more permeable. It is generally desirable to dry before extraction. In many cases it is sufficient to put the material for extraction direct into the Soxhlet tube, a little cotton wool (previously freed from fat) or glass wool being placed below and above it to prevent particles being carried over by the syphon. Finely powdered materials may be placed in a sort of thimble of filter paper, either specially made for the purpose (Schleicher and Schüll) or formed by folding over the end of a suitable test-tube. It is often convenient, instead of this, to use an inner tube formed by blowing a hole in the bottom of a large test-tube, which is closed with a tuft of cotton or glass wool.

The flask D is carefully weighed, and supplied with enough

On other forms of apparatus, compare Lewkowitsch, p. 148, 3rd edition.

of the solvent to fill the Soxhlet about once and a half, or twice; the apparatus is put together and heated till it syphons regularly once in 8 or 10 minutes, and this is allowed to continue till the material is judged to be exhausted. To test this, the flask may be removed and a second weighed flask substituted with fresh solvent. After completion of the extraction the solvent is distilled off both flasks and recovered, and the flasks are dried in the water- or air-oven till constant, which is facilitated by passing a gentle current of air or coal gas through them, and they are then cooled and weighed. If there is any gain in the second flask it is added to that of the first, but by noting the approximate number of syphonings required for each class of work, a second flask is usually unnecessary. Lewkowitsch uses a small tap on the outer limb of the syphon to draw samples and ascertain when the extraction is complete, and this is undoubtedly convenient, but adds materially to the cost of the apparatus. Where rapid work is required, it is often advantageous, after distilling off most of the solvent, to transfer the remainder to a weighed basin, rinsing the flask with a little more solvent, and evaporating to dryness on the water-bath in a draught closet. Absolute constancy is not to be expected, as on the one hand oxidation increases the weight, and on the other there may be slight loss from volatilisation.

Where the matter to be analysed consists mostly of fats, it will generally be possible, after evaporating the water (see below), to filter a sufficient part for further analysis through a weighed filter, which can then be completely extracted in the Soxhlet apparatus, and the insoluble matters determined. If the material is too thick to filter in this way, even in a warm water-oven, it may be thinned with a solvent sufficiently to enable it to be filtered, and this filtrate added to that from the extractor before distilling off the solvent. If the quantity of solid matter and the filter employed is small, it will often be sufficient to simply wash the filter with small quantities of petroleum ether, which in this case is the most convenient solvent, until a drop or two of the filtrate, evaporated on a watch-glass, no longer leaves a residue.

The insoluble residue of fats, and especially of dégras and other stuffing greases, may contain—beside organic matter accidentally present, and salts and acids from the process of manu-

facture—considerable quantities of soap, either added or formed by saponification of the fats, and mineral fillings, such as talc and china clay. Determination of the ash will, of course, give the mineral matter present. Soaps may be estimated from the amount of alkali found in the ash, or the fatty acids separated as in Section XIX. The methods of determining fats in egg-yolk and in dégras (pp. 337 and 352), may be referred to as good examples of dealing with rather difficult cases.

Determination of Water in Oils and Fats.—If the oil or melted fat is quite clear and transparent, it seldom contains any water or other impurities which for technical purposes need be removed before analysis, but sometimes, on heating, albuminous and gelatinous matters which have apparently been dissolved in the oil, are precipitated and separate.

To determine water, 2–3 grm. of the fat or oil is weighed into a platinum crucible without cover, and placed on a triangle in a somewhat slanting position. It is then gently and slowly heated by a small flame moved about beneath it. In presence of much water the liquid boils gently, but the last particles become superheated and escape with slight crackling and a tiny puff of smoke, indicating that the flame must be withdrawn. If the crucible be rapidly cooled by placing it on a block of metal, the whole estimation can be performed in fifteen minutes.*

Water may also be determined by drying on sand as described for egg-yolk, but the results are scarcely more accurate on account of oxidation, while the process is much more tedious. Where the quantity of water is not large, it is best simply to dry the fat at 110°–120° C., or even at 100°, in a small beaker with a stirring rod weighed in, stirring frequently till the weight is constant.

Where the determination of water and insoluble matters is not necessary, a sample may generally be purified sufficiently for analysis by simply filtering through a dry paper in a warm place, such as a water-oven.

Determination of Ash.—This is, as a rule, only necessary where the presence of salts or soaps is suspected, as in dégras. Some samples of oil and dégras contain traces of iron, which darken leather and give the ash a reddish tint, and may be estimated by the colorimetric process described on p. 40.

* Fahrion, Zeits. für angew. Chem., 1891, p. 172.

10 or 20 grm. of the fat is placed in a shallow platinum basin, which is slightly inclined, and the side only is heated by a small flame. The water first escapes without spurting, and the vapours then take fire and the fat burns quietly away (compare p. 288).

Detection and Estimation of Free Mineral Acids.—These (and especially sulphuric acid, which is extremely injurious to leather) are often present in dégras and sod oil. If the sample has a strong acid reaction, 25 grm. are boiled with 200 c.c. of water, the aqueous layer separated by a separating funnel and made up to an even quantity, of which an aliquot part is titrated with sodium carbonate solution, using methyl orange as indicator to prevent the interference of soluble fatty acids. In another part of the solution, the nature of the acid should be qualitatively determined.

B. PHYSICAL EXAMINATION OF FATS.

In default of marked chemical characteristics, the physical constants of fats are often of great value in their recognition and the detection of admixture, especially as in many cases they admit of easy determination on very small quantities. The approximate constants of many of the fatty matters which are most important to the leather manufacturer are given in the tables on pp. 349–350.

Specific Gravity.—That of oils is conveniently taken in an ordinary pycnometer, special care being taken as to temperature, as oils expand rapidly with heat. The outside of the bottle may be cleaned if necessary with a little petroleum ether before weighing; and after use it may be washed out with very weak caustic soda solution, then with distilled water, and carefully dried. The Sprengel tube is, however, to be preferred for accurate work, especially for small quantities. This is shown in Fig. 20, and consists in a U-tube of thin glass with two capillary ends, of which one, B, should be of about $\frac{1}{2}$ -mm. and the other, A, of $\frac{1}{4}$ -mm. bore. On the wider, a mark is made at M with a writing diamond. The tube is filled by connecting A with a glass bulb and rubber tube, and sucking the oil by B till it flows into the bulb. The ends are then wiped, the oil is brought to the requisite temperature by immersing the tube in water, and

adjusted to the mark by applying a piece of filter paper to the narrow end if oil is to be withdrawn, or a drop of oil on a glass rod if more is required. The tube is now weighed and the specific gravity calculated in the ordinary way; its capacity

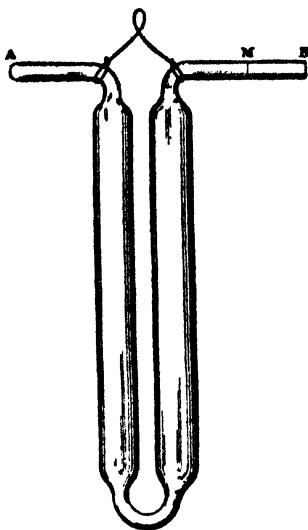


FIG. 20.

having been previously determined by weighing it first empty and then filled with water. Specific gravities are also conveniently taken by the plummet method, especially with Mohr's or hydrostatic balance (cp. p. 8). Hydrometers should only be used for very rough determinations.

The specific gravity of solid fats may be determined as on p. 7; but this determination has been largely superseded by that of the melted fats at 100° C., which is conveniently made in a Sprengel tube immersed in boiling water or steam in a beaker, or the neck of a flask, covered with a watch-glass, so that the capillary ends only

protrude. After boiling for twenty minutes, the volume of fat is adjusted, and the tube dried, cooled and weighed. Instead of the Sprengel tube, an ordinary small pycnometer may be used, suspended in steam with a wire sling. Any fat which is expelled is carefully removed from the hole in the stopper with a piece of blotting paper, while the flask is still in the steam. The flask is filled with liquid fat at a temperature below 100° C. The plummet method with Mohr's balance may also be used by placing the cylinder in a water-bath so arranged as to protect the balance from steam. The specific gravities are usually compared to that of water at 15° C. or 60° F. The sp. gr. of oils in glass vessels varies about 0.00064 for 1° C.; but in whale oil and liquefied fats the change is somewhat greater. Some chemists have determined the sp. gr. of oils at

100° C. as compared to water at the same temperature, which is easily done by weighing the tube filled with water at the same temperature as is used for the fat. Such determinations will be higher than those with water at 15° and fat at 100° in the proportion of 1.04 : 1. The sp. gr. of oils at 15° C., as compared to water at the same temperature, is about 0.00025 higher than when both are at 15.5° C.

A method of general applicability to very minute quantities of either solid or liquid fats at ordinary temperatures, is to suspend globules or small fragments in a mixture of strong and very weak alcohol, of which the proportions are varied till the fat globules neither sink nor rise to the surface. The sp. gr. of the liquid is then precisely the same as that of the fat, and can be determined in any convenient way. As the sp. gr. of alcohol solutions of known strength have been accurately tabulated and determined, this can be done volumetrically. An alcohol 50 per cent. by volume is of gravity 0.9335 at 15.5° C. (60° F.), and consequently just heavier than the heaviest oils, while a 70 per cent. alcohol is sp. gr. 0.8892, so that mixtures of these cover all oil gravities. Small volumes of alcohol are sufficient, and can be recovered by distillation. Globules of fat can be conveniently formed by dropping into cold 60 per cent. alcohol, or even on a damp glass plate, but they must be allowed to remain on blotting paper 18–24 hours before use to recover their original density (cp. p. 7). Air-bubbles, either adhering or enclosed, must be carefully avoided.

The Melting and Solidifying Points of fats and oils are often very characteristic, though from the fact that these bodies are usually mixtures of various constituents of different melting-points, the results are frequently somewhat indefinite. They are also in many cases considerably affected by the previous treatment of the sample. Thus, a tallow which has been melted at a high temperature has its melting-point considerably lowered, but regains its normal one on being remelted at a temperature little above that necessary for fusion and again cooled. In many cases the melting-point is varied by the proportion of free fatty acids present, and some sources of error are obviated by taking the melting or solidification point of the freed fatty acids in place of that of the original fat.

Prior to making the determination, the fats must be carefully

freed from water and solid impurities. This is generally sufficiently effected by keeping them gently melted for an hour or two, and filtering through dry paper. Fatty acids must be purified from alcohol and soluble acids by boiling for an hour with a large volume of water, and repeatedly washing with hot water. Fats do not regain their normal melting-point for at least twenty-four hours after solidification.

The determination of the melting-points of solid fats is usually made as follows. Thin tubes are drawn out to an open capillary point of 0.5-0.3 mm. bore, and sealed at the capillary end. A minute angular fragment of the solid fat is dropped into the tube, so that it rests on the shoulder of the capillary part, and the tube is attached with an elastic band to a delicate thermometer, so that the fat is level with the bulb, and immersed in a good-sized beaker of water, previously boiled to expel air-bubbles, which is heated by a small flame so that the temperature rises very slowly as it approaches the melting temperature of the fat. The water is continuously stirred with the thermometer or a separate stirrer, and the point is noted at which the angular fragment loses shape and adheres to the side of the tube. Sometimes the melting is gradual, and after incipient fusion the fat is still thick and turbid. In this case the temperature at which the globule becomes clear must also be noted. The method is applicable to pasty fats, like bone grease and dubbin, consisting of mixtures of liquid and solid constituents, but the temperature of clear fusion only can be noted.

In many cases, and especially in that of the fatty acids, the temperature of solidification is more definite than the melting-point, but is usually some degrees lower than that of complete fusion. If a solid fatty acid is melted and allowed to cool slowly while the temperature is observed, it will be noticed that the latter falls till the fatty acid begins to crystallise, and then rises some degrees from the latent heat of fusion which is liberated, remaining constant till solidification has taken place. With neutral fats this effect is less marked and definite, but at least a temperature can be observed which remains stationary for some little time during the solidification. As improved by Shukoff,* the observation is carried out as follows. A thin test-tube of about 3 cm. diameter is fixed by means

* Chem. Zeit., 1901, p. 99.

of a cork in a good sized wide-mouthed bottle, and a delicate thermometer capable of being read to 0.1 degree is fitted in it with a cork, so as to reach well down into the fat which is to be tested. The stem of the thermometer must be long enough for the graduation to be outside the cork at the point where it has to be read. The tube is next filled to a suitable height with the melted fat, which must not be too hot for the graduation of the thermometer, which is now inserted, and the whole allowed to cool slowly. As soon as the fat begins to show signs of turbidity, the vessel is vigorously shaken, and the

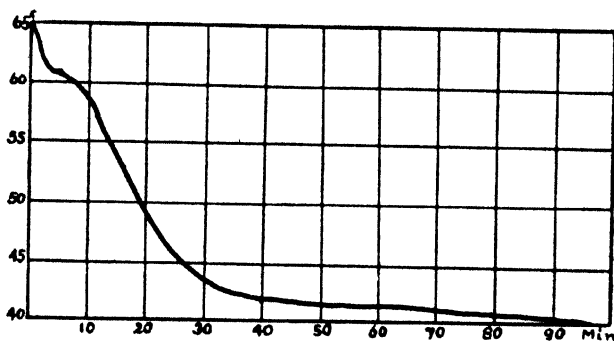


FIG. 21.—PARAFFIN AND MONTAN WAX.

temperature read from minute to minute. At the point of solidification, the temperature will either rise slightly, when the highest point reached is the required solidification temperature, or will at least remain constant for a short time at the required temperature. Of course, in fats and mixtures like dubbin, containing various constituents, there may be more than one solidification-point as this and the other constituent separates, and in such cases it is useful to continue the observations till the fat is fully solid, plotting them on a piece of curve-paper. A diagram obtained in this way by Graefe,* for a mixture of montan wax and soft paraffin is given as an example. Though the apparent melting-point by such methods as the capillary tube was 61.2° C., this is only indicated by a slight kink in the curve

* Chem. Zeit., 1904, p. 1144.

caused by the separation of most of the montan wax, and the real solidification-point of the remaining mixture is 42.6°C ., scarcely over that of the original paraffin. In this connection it may be noted that the true melting-point of such mixtures is always lower than the average of the constituents, and often lower than that of the one of lowest melting-point.

As applied by Dalican to the examination of the fatty acids of tallow, a similar method, known as the "titer test," is largely used both in this country and on the Continent for commercial purposes, and is carried out as follows:—

Fifty grams of fat is saponified with 40 c.c. of potash solution, sp. gr. 1.4 (or with 20 gm. of stick potash dissolved in 25 c.c. of water), and 40 c.c. of good alcohol, in a porcelain basin on the water-bath with constant stirring till the soap becomes pasty. It is then dissolved in a liter of water and boiled at least three-quarters of an hour to drive off the alcohol; water is added if necessary, and sufficient sulphuric acid to decompose the soap. The mixture is heated on the water-bath till the fatty acids separate in a clear oily layer, which is allowed to cool and solidify. The cake is perforated with a glass rod and the acid liquid poured off, and the cake is boiled repeatedly with fresh quantities of distilled water; and finally dried, melted at a low temperature and filtered through paper into a porcelain dish, in which it is allowed to solidify and stand over-night in a desiccator. It is then carefully melted on the water-bath at as low a temperature as possible, and its solidification temperature taken by the method of Shukoff. Dalican gives a table, reproduced in most books on fats, giving empirically the proportions of solid and liquid fatty acids, commercial stearic and oleic acids, corresponding to different solidifying-points.

The solidifying-point, or point of commencing turbidity, can be taken like the melting-point where only small quantities are available, allowing the water in the beaker to cool slowly, and noting the temperature at which the fat becomes turbid. In the case of oils, freezing mixtures may be used.

Index of Refraction.—Where a refractometer is available, it is desirable to determine the refractive index, as this can be rapidly done on even a single drop of fat, and in some cases furnishes valuable information. Many refraction constants are given in the tables on pp. 349–350. For the principles of this

measurement the reader is referred to elementary treatises on optics. The process differs somewhat with different instruments, and it is not necessary to describe it in detail, as working instructions are always provided. Zeiss's Butyro-Refractometer, a modification of the instrument invented by the late Prof. Abbe, is most convenient, and allows of determination over a wide range of temperatures. *

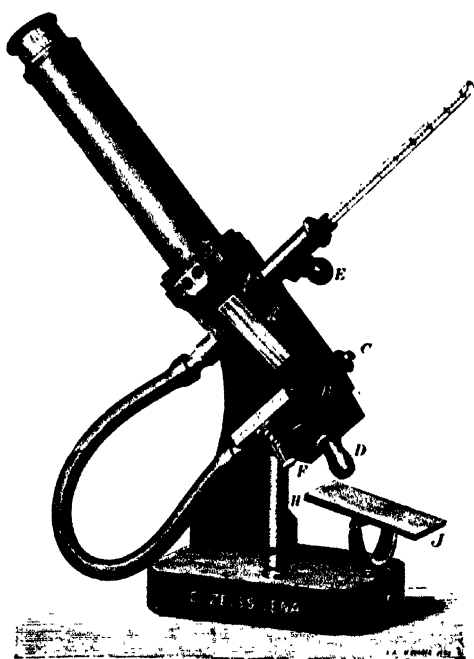


FIG. 22.

This instrument is shown in Fig. 22, and consists of two prisms of dense glass of acute angle, the face of the upper of which is shown at A, while the second is in the hinged part B. A drop or two of the oil to be examined is spread on the face of the lower prism, and the portion B is then turned on its hinge so that the oil forms a thin film between the faces of the two prisms. Light is now reflected by the mirror J through the

lower prism, and a portion passes through the oil into the upper prism, and thence to the eye-piece of the instrument, while another part striking the prism faces more obliquely, is "totally reflected" from the surface of the upper prism, and lost. The angle at which this takes place is dependent on the difference between the index of refraction of the oil and the glass; the nearer the two approach, the more oblique being the angle at which the light can pass through. On looking through the eye-piece the field of view is therefore divided into a light and a dark portion, the boundary of the light being sometimes sharp, but often shaded into a bluish or reddish fringe. The field is crossed by a scale divided into 100 parts, and on this the position of the boundary is read. As the scale is an arbitrary one, and only applies to the butter-refractometer, while some other instruments give the index of refraction direct, it is often desirable to convert it into terms of the latter, which is a well known physical constant. For this purpose the following table is given, derived by interpolation from the numbers given by Zeiss. In order to insure the constancy of the indications of the instrument, a "normal fluid" is supplied by the makers, which gives a sharp and colourless boundary, which at 15°C. corresponds exactly to 77.3 scale-divisions. By passing a current of water, warmed a degree or two above that required, through the nozzle D, and out at E, the temperature can be regulated to any required temperature up to 70°C. , so that the refractive index of fats and fatty acids of high melting-point can be taken. For this purpose it is desirable to order a thermometer reading to 65° or 70°C. , as that usually sent out with the instrument reads to 50°C. only. In addition to the refractive power, some information may be gained from the appearance of the boundary of the light part of the field. If it has a blue margin, it indicates that the dispersion of the liquid examined is higher than that of butter, for which the instrument is corrected, while an orange or red boundary indicates a lower dispersion. In cases where this margin is broad and undefined, a sodium flame (a Bunsen flame coloured yellow by salt, which may be introduced on a little spoon made of platinum foil, or by a tuft of asbestos moistened with salt solution) may be used as a source of light, when the margin will be sharp, and the refraction measured will be that of the sodium or "D" line. A red or orange glass fitted into grooves provided

TABLE FOR REDUCING SCALE OF BUTTER-REFRACTOMETER TO REFRACTIVE-INDEX.*

Scale.	Index.	Diff.	Scale.	Index.	Diff.	Scale.	Index.	Diff.	Scale.	Index.	Diff.
0	1'4220	80	25	1'4415	74	50	1'4593	66	75	1'4754	58
1	28		26	23		51	600		76	60	
2	36		27	30		52	06		77	66	
3	44		28	37		53	13		78	71	
4	52		29	45		54	19		79	77	
5	1'4260	80	30	1'4452	72	55	1'4626	66	80	1'4783	58
6	68		31	59		56	33		81	89	
7	76		32	67		57	39		82	95	
8	84		33	74		58	46		83	800	
9	92		34	81		59	52		84	06	
10	1'4300	78	35	1'4488	72	60	1'4659	64	85	1'4812	56
11	08		36	95		61	65		86	18	
12	16		37	503		62	72		87	23	
13	24		38	10		63	78		88	29	
14	31		39	17		64	85		89	34	
15	1'4339	76	40	1'4524	70	65	1'4691	64	90	1'4840	56
16	47		41	31		66	97		91	46	
17	54		42	38		67	704		92	51	
18	62		43	45		68	10		93	57	
19	69		44	52		69	17		94	62	
20	1'4377	76	45	1'4559	68	70	1'4723	62	95	1'4868	54
21	85		46	66		71	29		96	73	
22	92		47	73		72	35		97	79	
23	400		48	80		73	42		98	84	
24	07		49	86		74	48		99	90	
									100	1'4895	

below the lower prism may be substituted with convenience, but perhaps some loss of accuracy.

Messrs. Zeiss also manufacture another and more complete form of the Abbe refractometer, which, instead of an arbitrary scale, has merely cross-wires in the eye-piece, to which the shadow-edge can be brought by rotating the prisms, the move-

* The Refractive Index is given to the nearest decimal in the 4th place. The Differences represent the average value of the 4th and 5th places of decimals of the index for one scale-division, for the succeeding five divisions. With reading to 0'1 of a scale-division, the index is uncertain to about 1 unit of the 4th place.

ment being measured on a sector graduated directly to show refractive index. This instrument has the advantage of a much wider range than the butyro-refractometer, practically sufficient for the examination of all liquids, and is in addition, independent of the coloured fringes mentioned above, as it can be achromatised for liquids of any dispersion by a compensating prism fitted with a graduated circle, which enables the dispersion not merely to be compensated but measured. In some few cases this measurement can be utilised as a means of identifying oils.*

It is frequently necessary to correct the refractive index for small differences of temperature from the standard adopted. Tolman and Munson† have found that the change in ordinary oils and fats is very regular, being about 0.000365 for 1° C. If the butyro-refractometer is used, the scale number must be calculated to refractive index before applying the correction.

On examining the tables of oil constants, it will be noticed that in most cases the refractive index is roughly proportional to the gravity; and of course, like the latter, variable with temperature. Some additional information is obtained by calculating a specific refractivity independent of gravity and temperature, which may be approximately done by Gladstone and Dale's formula, $\frac{n - 1}{d} = c$, where c is the constant, n the refractive index, and d the specific gravity; and more accurately for the present purpose by the later formula of Lorenz, $\frac{n^2 - 1}{(n^2 + 2) d}$

For more detail as regards the application of this formula to oils, and a table for facilitating its calculation, the reader is referred to a paper of Procter's on "The Refractive Constant in Oil and Fat Analysis."‡ The main results are that gravity and refractive index are increased both by the presence or increased proportion of oxygen and of unsaturated linkages in an oil or fatty acid, but not in the same proportion, so that the refractive constant calculated by either of the formulæ given shows an increase from unsaturated linkage, and a diminution from oxidation. Thus, castor oil on the one hand and linseed and fish oils

* Cp. Procter and Holmes, *Journ. Soc. Ch. Ind.*, 1905, p. 128. "The Oxidation of Oils," part 1.

† *Journ. Amer. Ch. Soc.*, 1902, p. 754.

‡ *Journ. Soc. Chem. Ind.*, 1898, p. 1021; and *Collegium*, 1904, p. 153.

on the other, are among the highest both in gravity and refractive index, but are easily distinguished by refractive constant; that of castor being low (G and D 0.4987), from the presence of oxygen, while linseed and cod average about 0.518, from their unsaturated acids. On oxidation by "blowing" or exposure to air, as in chamoising, the unsaturated bonds are saturated by the absorption of oxygen, and in the case of a cod-liver oil examined the refractive constant fell to 0.4955. Thus the fall of this constant is a measure of oxidation. For further details on this point, the paper by Procter and Holmes above cited may be consulted. The refractive constant is a very valuable index of chemical constitution. It is very high in mineral oils, from the absence of oxygen, and in a less degree in sperm and other liquid (and solid) waxes, where the proportion of oxygen is low.

Specific Temperature Reaction (Maumené, Thomson, and Ballantyne).^{*}—When oils are mixed with concentrated sulphuric acid, complicated reactions take place with evolution of considerable heat. The amount of this is a measure of the chemical action, and depends both on the number of unsaturated bonds and that of OH-groups in the oil, while the "iodine value" (p. 306) depends on the former only. Hence, when an oil oxidises by exposure to the air, the heating with sulphuric acid is increased and the iodine number diminished. With close adherence to the prescribed method, the specific temperature reaction gives constant results, and is very rapidly performed, though it cannot claim the same amount of scientific accuracy as the iodine value. Both are in general terms an index of the proportion of drying oils and olein.

A deep beaker about 2 inches wide is fitted into a nest of cotton-wool in another beaker or cardboard box, so as to lessen the loss of heat.[†] 50 c.c. of water is measured into the beaker, and its temperature carefully determined with a delicate thermometer. 100 c.c. of the strongest sulphuric acid of exactly the same temperature is now slowly run in from a pipette, while the mixture is constantly stirred with the thermometer, and the

^{*} Journ. Soc. Chem. Ind., 1891, p. 233. This reaction might with equal justice be classed as a chemical one, but as the physical effect only is observed, it may conveniently retain its present place. (p. Twitchell, Journ. Soc. Ch. Ind., 1897, p. 1002; whose method, however, has not proved capable of giving accurate quantitative results.

[†] The Shukoff apparatus described on p. 292 may also be used.

highest temperature noted. If the acid is sufficiently strong for the purpose, the rise should amount to 42° – 44° C. The experiment is now repeated in precisely the same manner, with 50 grm. of oil in the same beaker, with the same acid and thermometer. The rise of temperature with the oil, divided by that with the water, and multiplied by 100 to avoid decimals, gives the "specific temperature." If any change whatever is made in the apparatus or acid used, the determination with water must be repeated. Equality of temperature is best attained by placing the vessels containing the acid and oil in a water-bath, which is generally at laboratory temperature, though with pasty fats, or where the reaction sets in with inconvenient slowness, it may be raised to 20° , or even more. It is best to use a pipette for the acid, drawn out to a fine point so that it requires about a minute to empty; and the temperature reached should not greatly exceed 60° C., or further reactions take place which render the results unreliable.* Since linseed, cod, and many other fish and seed oils, give a much higher rise, it is necessary to moderate the reaction, which is best accomplished by the addition of a proportion of heavy mineral oil, which gives but small rise of temperature, especially if it is previously purified by shaking with a little concentrated sulphuric acid and thorough washing. 20 grm. of linseed or fish oil to 30 grm. of mineral oil is generally a suitable proportion, and for semi-drying oils 30 to 20 grm. The heat evolved by the mineral oil cannot be determined directly, as the reaction is inconveniently slow, and its effect seems to vary with the proportion used. It must therefore be ascertained by experiment with the same proportion of a colza or rape oil, of which the rise of temperature has been carefully determined without mixture. If, for instance, the rise of temperature with 50 grm. colza amounts to 55° , that for 20 grm. should equal 22° , but a rise of 35° has been found for a mixture of 20 grm. colza and 30 grm. mineral oil. The rise due to the mineral oil is therefore 13° , and this must be deducted in each case where that quantity of mineral oil has been used, and the remainder multiplied by $5 \div 2$ before calculating the specific temperature.

The determination may be made with 25 grm. of oil and 5 c.c. of acid in a smaller beaker, and if divided by a water deter-

* Ellis, Journ. Soc. Chem. Ind., 1886, p. 150.

mination made under the same conditions, should give the same specific temperature as the larger quantities.

Olive or lard oil may be used instead of a mineral oil, and its evolution of heat may be directly determined, but a much larger proportion is required to produce the same lowering of temperature.

Specific temperatures of various oils are given on p. 349.

A similar temperature reaction, with the substitution of bromine for sulphuric acid,* has been employed by Hehner as a rapid substitute for the iodine value determination, but since the introduction of the more rapid volumetric methods of Wijs and Hanús (p. 308), these are generally to be preferred to either the bromine or the sulphuric acid reaction.

C. QUANTITATIVE ANALYSIS OF FATS.

In many cases where it is difficult or impossible actually to separate the various constituents of a fatty mixture, much information may be obtained from the determination of certain chemical constants or "values." The most important of these are: the "acid value" or number of mgr. of KHO required to neutralise the free acids of 1 grm. of the fat; the "saponification value," or mgr. of KHO required to form neutral soaps with the whole of the fatty acids of the same quantity; the "ether value," obtained by subtracting the acid value from the saponification value, and equivalent to the mgr. of KHO employed in decomposing and saponifying the neutral fats or glycerides; and the "iodine value," indicating the percentage of iodine absorbed by the fat, which is a measure of its unsaturated "bonds." These values form the basis of much of the quantitative analysis of fats, but a few of their more important applications may be mentioned here.

The Acid Value, when high, either denotes that the fat is rancid and decomposed, or that it contains additions of artificially produced free fatty acids, as, for instance, those produced by distillation, or in the recovery of grease from soap solutions. It is stated by Gadd that cod oil with a high acid value is particularly prone to "spue"; and by Wood, that such oils are

* Analyst, xx. (1895), 146; cp. also Journ. Soc. Chem. Ind., 1897, 87, 193, 209.

generally though not always unsatisfactory for chamoising. Oils and fats with much free acid are unsuitable as lubricants, as they corrode metals.

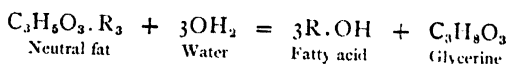
If the "mean molecular weight" or average combining equivalent of the free acids is known, their percentage is easily calculated from the acid value, by multiplying by this equivalent, and dividing by 561 (the eq. of $\text{KHO} \times 10$) (see below). The free acid, however, is not always of the same character as that remaining as undecomposed glyceride.

The Saponification Value, if known for any pure oil, affords the means of calculating approximately the amount of adulteration with mineral or rosin oils, which are unsaponifiable. Thus, pure cod oil has a saponification value of about 185. If a given sample only shows 166, we are justified in assuming that it contains about 10 per cent. of unsaponifiable matter. As, however, the saponification value varies a good deal even in genuine oils, it is always better, if the matter is of importance, to separate and weigh the unsaponifiable part (pp. 279, 309). It should be noted that distilled oils and greases and wool-fats contain naturally large proportions of unsaponifiable matter. The saponification value is a useful means of distinguishing different classes of oils. From it, the total fatty acids of the sample can be calculated if their molecular weight is known. That of stearic acid is 284, of palmitic 256, of oleic 282. The mean molecular weight of the mixed acids of tallow is about 275, and of cod-liver oil, according to Dieterich, about the same. The mean molecular weight of the free acids, insoluble in water, is easily determined from the saponification (or acid) value of a small quantity of the washed acids recovered after saponification (p. 306). If M = mean molecular weight, and K = saponification value, $M = \frac{56100}{K}$. In

the case of fatty acids, the acid value should be identical with the saponification value unless lactones (anhydrides of the hydroxy-fatty acids) are present, which is probably never the case in natural fats, but may occur where they have been treated with sulphuric acid or other dehydrating agents, or distilled at high temperatures. In this case, the fats have what is called a "permanent ether value," as the lactones are saponified by hot potash solution, but not by cold aqueous potash; and again partially take their anhydride form, if the soap so formed be

decomposed by acids (cp. p. 317). According to Ruhsam, they are found in dégras.*

The Ether Value gives, as has been stated, the amount of potash corresponding to neutral glycerides of the fatty acids. As most natural fats consist exclusively of glycerides with more or less free acid, the percentage of glycerin may be found by multiplying the ether value by 92, the molecular weight of glycerin, and dividing by $561 \times 3 = 1683$. Similarly, the fatty acids are found by multiplying by their molecular weight, and dividing by 561. The sum of the fatty acids and glycerin will be more than 100 per cent. by rather over 6 per cent., on account of the hydration of the acids and glycerin, as will be seen by the following equation, R being the radical of any fatty acid, R.OH :—



The Iodine Value is a measure of the acids with unsaturated carbon atoms, and of course where only one such acid is present, as oleic in tallow or lard, its amount can be calculated from the value. The theoretical iodine value for oleic acid, with which the experimental closely agrees, is 90.07, and for olein, its triglyceride, 86.2. The percentages may therefore be found by the following formulæ, given by Benedikt, I being the iodine value :—

$$\text{Percentage of Oleic acid} = \frac{100 \times I}{90.07} = 1.1001 \times I.$$

$$\text{Percentage of olein} = \frac{100 \times I}{86.2} = 1.1102 \times I.$$

Where several unsaturated acids are present, their quantities cannot be calculated in this way ; but the iodine value will still enable us to calculate approximately the proportion of two constituents for which it is known. Thus a dubbin composed of equal parts of a cod oil of 160, and a beef tallow of 40 iodine value, would have itself an iodine value of 100.

We may also safely conclude that any oil with an iodine value above 86 must contain glycerides with more unsaturated bonds than oleic acid, and hence probably of a drying character.

* 3 Jahresbericht der Deutschen Gerberschule, Freiberg, p. 11.

The converse, however, would not necessarily be true, on account of the probable presence of saturated fats, such as stearin and palmitin.

Determination of Acid-Value.—In a wide-necked conical flask of 250–300 c.c. capacity put 50 c.c. of good alcohol, and 1 c.c. (or 20 drops) of a 1 per cent. alcoholic phenolphthalein solution; and add a drop or two of $N/10$ KHO, or NaHO till it is faintly pink. Weigh the oil or fat in a small beaker with a glass rod, transfer about 3 gm. (or more if the oil is known to be nearly neutral) to the flask, and determine the weight taken by re-weighing the beaker.

Add $N/10$ KHO or NaHO from a burette very cautiously to the flask till the pink colour no longer disappears at once on vigorous shaking, and note the quantity used. If solid fats are titrated, the flask must be gently warmed, so that the fat is kept just fused during the operation. The acid value is obtained by multiplying the number of c.c. of $N/10$ alkali by 5.61, and dividing by the weight in grams of oil or fat.

In cases where the quantity of oil available is very small, it is often convenient to use standardised alcoholic potash, in which case the same quantity of fat can be used for determination of saponification value (see p. 306).

Determination of Saponification-Value (Köttstorfer).—A solution of alcoholic potash is made by dissolving about 8 gm. of potash "pure by alcohol" in 10 c.c. of water, and making up to 250 c.c. with good nearly absolute alcohol. Methylated spirit may be used if it is previously purified by shaking with powdered permanganate till strongly coloured, and after standing some time to deposit the hydrated manganese peroxide, is distilled off potassium carbonate, the first and last portions being rejected for commoner purposes. Another method, recommended by J. Carter Bell,* is to place 500 c.c. of strong methylated alcohol in a flask of 1000 c.c. capacity, and to dissolve in it 25 gm. of stick potash. 250 gm. of lard or other saponifiable fat is now added, and the mixture heated on the water-bath with vertical condenser till saponification takes place, when the condenser is turned downwards and about 450 c.c. of alcohol distilled off. Alcohol sufficiently pure for use gives a colourless solution of potash, which on keeping (in the dark), or on boiling, only turns

* Journ. Soc. Chem. Ind., 1893, p. 236.

yellow and not brown. Ordinary commercial methylated spirit contains a proportion of light petroleum spirit, which if sufficiently volatile does not interfere with the use of the alcohol even for the separation of unsaponifiable matter. Fractions of petroleum of higher boiling-point might probably be removed by rectifying the spirit off paraffin or vaseline (p. 286), or very likely off lard.

Mr. T. Mann purifies methylated spirit by the use of meta-phenylenediamine hydrochloride, of which 10 grains in fine powder is added per liter. The mixture is shaken up from time to time during two or three days, and then distilled, preferably with the aid of a fractionating column, about nine-tenths of the spirit being allowed to come over. Alcoholic soda of N/2 strength made up with methylated spirit purified in this way does not discolour on boiling, and is still quite fit for use after keeping a month in daylight. In fact it is only very slightly inferior to that made with the best rectified spirit.

The alcoholic solution of potash is allowed to stand for twenty-four hours, to deposit potassium carbonate, and is then transferred (if necessary filtering through glass-wool to obtain a clear solution) into a bottle fitted with an india-rubber cork, through which is passed a 25-c.c. pipette closed at the upper end with a piece of rubber tube with a pinchcock. It should be kept in a dark and not too cold place.

A quantity of oil or fat not exceeding 2 grm. is transferred as before into a flask of 150–200 c.c. capacity, which should be of Jena glass (or other hard glass not easily attacked by alkali), and 25 c.c. of the alcoholic potash is added, allowing the pipette always to deliver the same number of drops after it had ceased to run in a stream, so as to secure an absolutely constant quantity. A second 25 c.c. is run in the same way into a similar flask as a blank test, both flasks are closed with corks fitted with vertical glass tubes of perhaps 50 cm. long and 0.4 cm. bore, which should be cut or broken slanting at the lower end to facilitate dripping. The flasks are now placed in a shallow water-bath already boiling, and simmered for half an hour, the contents of each flask being frequently shaken with a rotatory motion. 1 c.c. of 1 per cent. phenolphthalein solution is now added, and the liquids carefully titrated back with accurately N/2 HCl, great care being taken not to overstep the point of neutrality.

The difference in the two results represents the potash consumed in saponifying the fatty acids, both free and combined. Each c.c. of the $N/2$ HCl corresponds to $(56.1 \div 2)$ mgr. of KHO, which multiplied by the number of c.c. of acid used, and divided by the weight of the fat in grams, gives the saponification value.

In some cases, where only a small quantity of the fat is available, it is desirable to determine both the acid and saponification values on one weighed quantity of fat. This is easily done by using alcoholic potash of known strength for titrating the acid value, and then adding the usual 25 c.c. of alcoholic potash and saponifying. In this case the potash consumed in saponifying will give the ether value direct. If 3-4 grm. of fat be used with 50 c.c. of alcoholic potash for the saponification, it is possible to shake out the unsaponifiable matter as on p. 309, and afterwards to separate the fatty acids and examine them on a single portion of fat.

Determination of Iodine Value.—The original method of Hübl has been superseded in most cases by the modifications of Wijs and Hanûs, but is given here since many of the published data have been obtained by it, the points in which it has been varied by Wijs and Hanûs being noted subsequently.

Hübl's Method.—The following solutions are required :—

1. Iodine Solution (Iodine and Mercuric Chloride). 25 grm. of pure iodine are dissolved in 500 c.c. of pure "absolute" alcohol. Methylated spirit must not be used. 30 grm. of pure mercuric chloride are separately dissolved in a similar quantity of the same alcohol, and, if necessary, filtered. The solutions are best kept separately, but should be mixed in equal parts at least twelve hours before use, as considerable loss of free iodine takes place soon after mixing, but afterwards much more slowly. Some operators, however,* prefer to mix only at the moment of using; and correct results may be obtained in this way if a blank test is made under precisely the same conditions to establish the strength of the iodine solution. The mixed solution is best kept in a bottle fitted with a 25 c.c. pipette as described for alcoholic potash.

2. Sodium Thiosulphate Solution. About 25 grm. per liter. If pure thiosulphate is at hand, a solution of 24.8 grm. per liter will be accurately decinormal. As, however, it does not keep

* Fahrion, Chem. Zeit., 1892, p. 862.

permanently, the strength must be determined from time to time. This is most conveniently done with standard solution of potassium iodate (to be had pure of Merck), but potassium bichromate may also be used (p. 258). One molecule of either of these salts liberates 6 atoms of iodine from potassium iodide in presence of HCl. Therefore 3.566 grm. of KIO_3 or 4.91 grm. of $\text{Cr}_2\text{K}_2\text{O}_7$ made up to 1 liter, is decinormal as regards iodine of which it is equal to 12.7 grm. per liter, and 20 c.c. of either of these solutions allowed to stand for half an hour in a stoppered bottle with 10 c.c. of 10 per cent. potassium iodide solution and 5 c.c. of strong hydrochloric acid will liberate 0.254 grm. iodine, and equal 20 c.c. of decinormal thiosulphate.

3. Potassium iodide solution is made by dissolving 100 grm. in a liter of water. Commercial iodide not unfrequently contains iodate, which liberates iodine in presence of HCl. If this is the case, the amount of iodine liberated must be determined and allowed for. Hydrochloric acid also occasionally contains traces of free chlorine, to which the same remarks apply.

4. Chloroform should be pure, and not absorb any iodine; but if the strength of the iodine solution is always ascertained by a blank test, in which the same quantities of potassium iodide and chloroform are used as in the actual determination, any errors due to these sources will be cancelled.

5. Starch solution is best prepared fresh for each analysis by mixing $\frac{1}{2}$ grm. of starch into 100 c.c. of cold water, and raising to a boil with constant stirring. The clear solution is used.

The determination is carried out as follows:—0.15 to 0.18 grm. of drying or fish oil, 0.3 to 0.4 grm. of a non-drying oil, or 0.8 to 1 grm. of a solid fat is weighed accurately into a bottle of 500 to 800 c.c. capacity, having a well-ground stopper. 10 c.c. of chloroform is added, and 25 c.c. of iodine solution measured in with the same precautions as in measuring the alcoholic potash for the saponification value. If the mixture, after shaking with the iodine solution, is not clear, more chloroform must be added. If after a short time its deep brown colour shows signs of becoming pale, another 25 c.c. of the iodine solution must be added. The bottle is allowed to stand four to six hours protected from the light (some chemists allow 18 hours), after which 10 c.c. of potassium iodide solution and about 300 c.c. of water are run in. Should a red precipitate of mercuric iodide

be formed, it indicates an insufficiency of potassium iodide, of which more must be added. The mixture is now titrated with thiosulphate solution, which is run into the bottle and well shaken after each addition till the chloroform layer is only faintly coloured. A few drops of starch solution are now introduced, and the titration continued very cautiously till the blue colour becomes permanently discharged. A blank test should be made at the same time with the same quantity of reagents, but without the fat, and similarly titrated, and the difference between the two will give the thiosulphate solution equivalent to the iodine absorbed by the fat, from which the iodine value is calculated by multiplying the corresponding weight of iodine by 100, and dividing by the weight of fat employed. If the reagents are all perfectly satisfactory, it is sufficient to titrate 25 c.c. of the iodine solution alone at the same time to obtain the original strength, but it is safer to carry out the blank experiment.

Methods of Wijs and Hanús.—These methods are simpler, more rapid, and much cheaper, and the solutions are much more permanent than that of Hübl. The most convenient way of making the Wijs solution is to dissolve 5 grm. of iodine trichloride in 500 c.c. of glacial acetic acid, and to add 5.4 grm. of iodine, which dissolves to a clear port wine colour. The Hanús solution is similarly made by dissolving 6.6 grm. of iodine in 500 c.c. of glacial acetic acid, and adding 1.5 c.c. (about 4.2 grm.) of bromine to the cooled solutions. Both these solutions keep very well. Both are used in the same way and give approximately equal results, those with Wijs, on the whole, being slightly the highest, while the Hanús solution is intermediate between that and the original Hübl. For this reason, and because the solution is most readily prepared, the Hanús method has mostly been used in the author's laboratory. The process is carried out as follows:—

A suitable quantity of oil, varying from 0.1 grm., for fish or drying oils, to 0.4 grm. in the case of non-drying oils, is weighed into a stoppered bottle, and dissolved in 10 c.c. of pure chloroform, and 25 c.c. of the iodising solution (either Wijs' or Hanús') is run in, accurately measured, from a burette or pipette. It is found best to let the mixture stand for 1 hour before titrating, though for non-drying oils, considerably less time would be sufficient. After standing the necessary time, 10 c.c. of 10

per cent., potassium iodide solution is added, and the iodine liberated is titrated with N/10 thiosulphate solution as described above, employing starch towards the end of the reaction. The first disappearance of the blue colour is to be taken as the end, though it may afterwards reappear through oxidation or dissociation, and it is therefore desirable that the titration should be done as rapidly as possible, in order to avoid the change taking place during the process, and so introducing an error. The following table gives the results of comparison between the three methods which have been mentioned.

Name of Oil.	Hübl.	Hantz.	Wijs.
Pale seal	117·5	120·7	124·8
Whale	120·2	120·6	123·7
Olive	82·3	81·9	83·4
Castor (cold drawn)	82·6	84·4	85·6
Dogfish liver	134·7	141·2	143·2
Arachis (earthnut)	91·8	91·6	93·4
Arctic shark	89·0	93·8	98·9
Pale rape	103·0	101·9	102·1
Coast cod	148·5	147·5	154·6
Newfoundland cod	144·8	150·0	154·7
Linseed	174·8	174·5	177·3
Cottonseed	108·5	107·0	110·0

Determination of Unsaponifiable Matter.—In the cases of oils and fats which are not likely to contain wool-fats, distilled "olein," or sperm or shark oil, 10 grm. are weighed into a flask, 50 c.c. of alcohol and 5 grm. of stick potash dissolved in 5 c.c. of water are added, and the flask is boiled for one hour with inverted condenser; 50 c.c. of water are now added, and the solution is allowed to cool. It is then poured into a stoppered separating funnel of 150–200 c.c. capacity, and 30–50 c.c. of petroleum ether (boiling below 75°C.) are added, and gently mixed with the soap solution with a rotatory motion, avoiding at first violent shaking. If, on allowing the mixture to rest, the ether layer readily separates, somewhat more agitation may be given, but care must be taken to avoid the formation of a permanent emulsion. The mixture is now allowed to rest and separate (if

necessary for some hours), and the soap solution is run back into the flask in which it was saponified, where, to save time, it may be tightly corked and shaken with another portion of ether, and this time somewhat more vigorously, as the bulk of unsaponifiable matter is already removed, and allowed to rest while the ether in the separating funnel is washed with water. Care must be taken that, before washing, the *whole* of the soap solution is removed, it being much less injurious in this stage to run off a drop of ether with the soap than to retain even a trace of the latter. 50 or 100 c.c. of water are now added to the contents of the funnel which are even more cautiously shaken than in the first instance, allowed to separate, and the water run off into a large flask or beaker, taking care in this case to avoid running away any of the ether. This washing is repeated twice, but the second and third time, the mixture being free from all but a trace of soap, may be vigorously shaken. Should an emulsion be formed which separates with difficulty, the addition of a few cubic centimetres of alcohol will often break it up. The washed ether is now run into a dry flask and well corked. The soap solution is poured back into the separating funnel; a further portion of petroleum ether is added, and the process just described is repeated for a second and third time, the washed and separated ether being added to that in the corked flask. After the whole of the petroleum ether solution has remained in the dry flask long enough to deposit particles of water which it retains, it is poured into a weighed flask, the first flask being rinsed with a little fresh petroleum ether, which is added to the rest. The bulk of the ether is now distilled off and recovered, and the unsaponifiable matter dried to approximate constancy in the water oven, and weighed. *Volatile* unsaponifiable matter is, of course, lost, and in the case of mineral oils it is not well to push the drying too far.

Wool-fat, spermaceti, waxes, and sperm, dolphin, shark-liver, and some other marine animal oils consist wholly or in part of compounds of fatty acids with higher alcohols instead of glycerin, and are usually only imperfectly saponified by the ordinary treatment with alcoholic potash. Complete saponification can be effected by digesting with double-normal alcoholic potash under pressure at 105° to 110° C., or by treatment with sodium ethoxide (prepared by dissolving 5 grm. metallic sodium in

100 c.c. of absolute alcohol), with subsequent digestion on the water-bath. The most generally practical method is to heat with 2 N alcoholic potash in a copper flask or tube with screw stopper, or in a small soda-water bottle with wired cork. The latter should be enclosed in several thicknesses of canvas in case of explosion, and placed vertically in an iron pan with saturated salt solution, which is very slowly heated to its boiling point (about 109° C.), and maintained at this temperature for one hour. If an accurately measured quantity of potash solution be used, the saponification value can be simultaneously determined.* After complete saponification, the higher alcohols remain as "unsaponifiable matter," and can be shaken out in the usual way. Sperm oil and spermaceti yield about 40 per cent. of these alcohols, and wool-fats less.

In general, the "unsaponifiable matter" in wool-fats and recovered greases is determined simply by saponification in the ordinary way, and of course includes the undecomposed waxes. For many purposes this is sufficient, since the proportion saponified at the ordinary pressure seems practically constant, amounting to 40 or 45 per cent. of the total fats. Where difficultly saponifiable matters are suspected, it is desirable to continue the saponification for two hours, and, in the case of marine oils, to shake out with ethyl-ether instead of petroleum, since it has been observed by Lewkowitsch† that the higher alcohols are not easily taken up by petroleum ether. Where ethyl-ether is used, the greater part of the alcohol must be boiled off before shaking up, and the soap solution made up with water, but a little alcohol may be subsequently added if needed to break up emulsions. It will frequently happen with fats of the class named that a flocculent layer of difficultly soluble soaps of the higher acids will form below the ethereal layer. These must be retained with the soap solution. Flocks of similar soaps are often suspended in the ether layer, and will generally separate with the particles of water in the dry flask, but must otherwise be removed by filtration, and the filter washed with ether. Ethyl-ether dissolves larger proportions of neutral soaps than petroleum ether. Gawalowski‡ states that neutral soaps are quite insoluble in petroleum ether, and recommends approximate neutralisation

* *Op. Herbig, Ding. Polyt. Journ., 1894, cxcvii. p. 66.*

† *Journ. Soc. Chem. Ind., 1896, p. 14*

‡ *Zeit. Anal. Chem., xxvii. p. 330.*

with calcium chloride, and addition of sodium hydrogen carbonate with subsequent boiling. Good results may also be obtained by carbonating the caustic alkali by passing CO_2 through the solution, or by neutralisation to phenolphthalein with dilute acid, and the subsequent addition of a small quantity of sodium carbonate to restore alkalinity and combine with any trace of freed fatty acids. Soap may be detected in the "unsaponifiable" by incinerating, when it will be indicated by the presence of alkali in the ash, from which its amount may be approximately calculated.

In place of shaking out, unsaponifiables may be extracted from the dried and powdered soap in the Soxhlet apparatus, and Baldracco* recommends this method for the analysis of *dégras*. Details of this procedure will be found on p. 342.

It is often of importance to determine the nature of the unsaponifiable matter. Apart from the presence of wool-fat, mineral oil, and less frequently rosin oil, added by way of adulteration, are by far the most common. They can generally be recognised by their liquid consistence, colour and smell. Rosin oil is easily distinguished from mineral oil by its much greater sp. gr. and higher refractive index. Mineral oil ranges from 0.850 to 0.920 sp. gr. and 1.4776 to 1.4980 ref. ind.: while in rosin oil, these are from 0.960 to 0.990 and from 1.5274 to 1.5415 respectively. Rosin oils are miscible with acetone in all proportions, but mineral oils require several times their volume for solution. Both classes of oil are generally fluorescent, but a feeble green "bloom" or fluorescence is often noticed in animal and vegetable oils of undoubted purity, while that of mineral oils is frequently masked by addition of nitronaphthalene and other nitro-compounds. In this case it is restored by washing the oil with concentrated sulphuric acid. The ordinary colour tests for rosin oil are useless in presence of liver oils, or wool-fat, since very similar colours are produced by the cholesterol and lipochromes present in these fats, but in most cases resin acids may be detected among the fatty acids by the tests given on p. 316.

The presence of large quantities of cholesterol is characteristic of wool-fat, but as this body, together with lipochromes, occurs in liver oils, the same remarks apply, and its qualitative detection is not of much value. When the more or less solid consistence,

* Collegium, 1904, p. 333.

the smell, or other causes lead to suspicion of the presence of wool-fats, the most satisfactory method is to resaponify the "unsaponifiables" obtained in the ordinary way, either under pressure, or by the aid of sodium ethoxide (p. 310). An additional amount of fatty acids and corresponding diminution of unsaponifiables, indicates with certainty the presence either of wool-fat, or of liquid waxes from some other source, and probably with further experience, it will be found that the amount of wool-fat can be inferred from the quantity.

If the unsaponifiable matter is small in quantity, and more or less crystalline, it probably consists mainly of cholesterols and isocholesterol, or, in the case of vegetable oils, of the closely allied phytosterols. These bodies may be detected by dissolving the unsaponifiable matter in a little chloroform, and shaking with an equal volume of concentrated sulphuric acid. Cholesterol and phytosterol colour the chloroform layer red or purple. Isocholesterol causes a strong green fluorescence in the sulphuric acid, and gives a yellowish tint to the chloroform layer which often masks the purple or pink due to cholesterol. Somewhat similar colorations to that due to cholesterol are also given by the "lipochromes" present in liver oils, and reddish colorations by resin acids (see p. 316); but the latter should be removed by saponification. Phytosterol may be distinguished from cholesterol by difference of melting-point and crystalline form of the two bodies and their acetates, under microscopic examination, and their recognition is important in the detection of mixtures of animal and vegetable oils, but for details the reader must be referred to the books of Lewkowitsch and others.

The high alcohols present in wool-fat and other solid and liquid waxes may also be present among the unsaponifiable matters, as well as undecomposed waxes, if the saponification has not been done under pressure. It is not easy to separate these from the cholesterols, and the reader must be referred for the best methods to Lewkowitsch ('Oils, Fats and Waxes').

Paraffin and ceresin may also be present among the unsaponifiable solids, and may be separated from cholesterol and other alcohols by digestion for two hours at 100° C. with acetic anhydride or less accurately by washing with ordinary alcohol, in both of which the paraffins are practically insoluble. The method is also applicable to liquid paraffins. If cholesterols or other

alcohols are present in large quantity, their acetylated products usually separate from the acetic anhydride as it cools, or in any case by pouring the solution into cold water.

Fatty Acids.—The soap solution, after removal of unsaponifiables and boiling off the alcohol, may be decomposed with dilute sulphuric acid, and the fatty acids separated as on p. 278. Care must be taken, in boiling off the alcohol, that the vapour which at first contains considerable petroleum ether, does not catch fire, and the operation is best performed on the water-bath; or a distillation flask and condenser is used, and the alcohol recovered. If it is desired to determine the acids quantitatively, it is convenient to wash them with hot water in a separating funnel, the wash waters being passed through a weighed filter of close texture, on which the fatty acids are finally collected. The wet filter is now placed on the top of a small tared beaker and dried in the water-oven to approximate constancy, when the greater portion of the fat will filter through, and is ready for further examination. The acids thus obtained are, of course only those insoluble in water, any soluble (volatile) acids present being retained in the wash water. The percentage of insoluble acids is known as the "Hehner value." For the determination of the volatile and soluble acids ("Reichert-Meißl value") see Lewkowitsch.

Separation of oxidised fatty Acids (Dégras-Former).—Linseed and fish oils yield, on oxidation, products of which the fatty acids are insoluble in petroleum ether, but soluble in alcohol. The determination of these oxidised acids in linseed varnishes and japans, affords a criterion of the amount of oxidation they have undergone, while in dégras, in which they are formed during the chamoising process, their presence, according to Simand, is the cause of its readiness to form an emulsion with water and to a certain extent a measure of its genuineness and quality, and they are hence styled by him "dégras-former" (Degrasbildner). Their importance in this respect has, however, been much over-rated, as they can be formed in any quantity by the artificial oxidation of fish-oils. They may be determined in the soap solution, after extraction of the unsaponifiables, in the following manner. After boiling off the alcohol, the soap is dissolved in hot water and the solution is transferred to a large separating funnel and decomposed with slight excess of dilute sulphuric or hydro-

chloric acid, which should be roughly standardised against the quantity of potash used in saponification. After cooling, the mixture is vigorously shaken for five minutes with 100 c.c. of petroleum ether, and the funnel set aside for several hours till both the ethereal and aqueous layers have become clear. The aqueous solution is then run off, when the oxidised acids will usually adhere to the sides of the funnel, and the ethereal layer can be poured from the top of it without disturbing them. They are washed several times with petroleum ether, and dissolved in hot alcohol, which is filtered, evaporated to dryness in a porcelain basin (which should not be more than half filled, as the solution readily creeps over the sides) and finally dried for one hour at 100–105° C. and weighed. The ethereal solution, after shaking a few times with water to remove mineral acid, may be distilled off, to recover the remaining fatty acids for further examination. Where only determination of oxidised fatty acids is required, as is frequently the case with *dégras*, the process may be simplified as follows (Maschke). 5–7 grm. of the *dégras* are weighed into a porcelain basin; 0.5–1.0 grm. solid caustic soda, or rather more caustic potash, is added, together with 50 c.c. of good alcohol, and if necessary a few drops of water to complete the solution of the alkali, and the whole is slowly evaporated nearly to dryness on the water-bath with occasional stirring. The soap is then taken up with water, and decomposed with acid, and after separating with petroleum ether as above described, the alcoholic solution of oxidised acids is evaporated, and weighed in the same basin in which the saponification took place. The method is not to be recommended for the determination of small traces of oxidised acids in easily oxidisable oils, which would be liable to further oxidation in the open saponification.

According to Simand, genuine *dégras* should contain not less than 15–20 per cent. of these oxidised acids calculated on the dry weight. It may be noted (cp. p. 299) that as the oxidised acids increase, the iodine value falls; and in all probability the acetyl value, being a measure of the hydroxyacids, correspondingly rises. The resinous exudation on leather known as “spueing,” “gumming,” or “frying,” is due to the production of these oxidised acids on the surfaces of the leather, and therefore fish oils of very high iodine value, such as menhaden oil, are specially liable to produce it, but it does not seem to be favoured by the presence of ready formed oxidised acids as in *dégras*.

Most artificial dégras is made with oxidised or "blown" oils, and it is probable that such oils may find other useful applications in currying. There is no known reason why a dégras formed by direct oxidation should be in any way inferior to the actual product of chamoising.

Determination of Resins.—Rosin, or ordinary pine resin, is a usual constituent of soaps, and is frequently found in stuffing greases and dégras, either as an intentional addition, or as a constituent of rosin oil. Rosin consists practically of the anhydrides of abietic, and perhaps other acids, and hence is found after saponification among the fatty acids. It may often be recognised by taste and smell where the ordinary colour reactions are inapplicable. It may be detected among the fatty acids by the Liebermann-Storch reaction (in absence of liver oils, which contain lipochromes which give a violet coloration with sulphuric acid). Cholesterols, which give a similar colour-reaction, must first be removed with other unsaponifiable matters by shaking out the soap solution, as on p. 309. The separated fatty acids are dissolved in a small quantity of acetic anhydride. The solution is then cooled, and a few drops of sulphuric acid of S.G. 1.53 (about 55 c.c. of concentrated S.G. 1.84 acid made up to 100 c.c.) is gently run in. In presence of rosin a transient reddish violet coloration is produced. In absence of cholesterols the test may also be used to detect rosin oil, and even when both have been removed by shaking out, the fatty acids may show traces of rosin.

Rosin is probably best estimated by the volumetric modification of Twitchell's method,* though the results must only be taken as approximate to the quantity of crude commercial rosin used. It is carried out as follows: 2–3 grm. of the mixed acids are weighed accurately, and dissolved in a flask in 30 c.c. of *absolute* alcohol. The flask is cooled by immersion in cold water and *dry* HCl gas is passed in till it ceases to be absorbed, which occurs generally in about three-quarters of an hour. The flask is allowed to stand for one hour and then diluted with 150 c.c. of water, and boiled till the aqueous layer becomes clear. After cooling, the contents of the flask are transferred to a separating funnel, the flask being repeatedly washed with ether which is

* See Benedikt and Lewkowitsch, p. 195; Wilson, Journ. Soc. Chem. Ind., 1891, p. 952.

united with the rest. The acid layer is now run off, and the ethereal is either washed with repeated changes of water and vigorous shaking till the aqueous layer remains perfectly neutral, or decinormal alkali is cautiously added till it remains neutral to methyl orange. After running off as much of the water as possible, 50 c.c. of alcohol is added, and the solution of resin acids is titrated with standard alkali in presence of phenolphthalein as in determining the "acid value" (p. 304). Each c.c. of normal alkali is approximately equivalent to 0.346 grm. of rosin. In the determination of other resins an equivalent must be found experimentally. The process is based on the fact that fatty acids combine with alcohol in presence of dry HCl to form neutral ethylic esters, while the rosin acids are practically unaltered.

Lactones are the so-called "inner" or cyclical anhydrides of hydroxyfatty acids. When a hydroxyl is substituted in a suitable position for one of the hydrogen atoms in the hydrocarbon nucleus of a fatty acid, it becomes capable of combining with the hydroxyl of the carboxyl group of the same molecule (just as the hydroxyl of another alcohol might unite with it to form an ordinary ethereal salt or "ester"), with elimination of a molecule of water derived from the hydrogen of the carboxyl group and the alcoholic hydroxyl. Such a lactone may be likened to a snake with its tail in its mouth, and is devoid of acid properties, behaving like an ethereal salt. It is saponified by caustic alkalis in the ordinary way, the original hydroxyacid being re-formed as an alkali salt; but as soon as it is liberated again from the base, it loses one molecule of water, and recombines with itself to form a lactone. Fatty acids containing lactones have thus a "permanent saponification value" and "permanent ether value," from which the amount of lactone may be calculated. In some cases, however, this reformation is only partial, and by repeated saponifications the amount of lactone is often reduced or converted into permanent free acid. It is not every hydroxyfatty acid which is capable of forming a lactone. The combination takes place most readily when the hydroxyl occupies the γ position of the carbon chain in reference to the carboxyl group, and thus forms a complete ring when combined with the latter group. When an unsaturated acid like oleic is acted on by concentrated sulphuric acid, or

heated with zinc chloride, compounds are formed which, on being boiled with water or weak acid, split up and leave the oleic acid with the addition of a hydroxyl and a hydrogen in place of its unsaturated bond, thus converting it into hydroxystearic acid. A portion of the acid so formed is usually γ hydroxystearic acid, which at once forms stearolactone ($C_{18}H_{34}O_2$). Thus lactones are usually found in turkey-red oils prepared by treating oils with sulphuric acid, in candle material by Schmidt's process (heating oleic acid with zinc chloride), and in other cases where hydroxystearic acids are produced. It has hence been found by Lewkowitsch in distilled stearines, and by Ruhsam in dégras.

The Acetyl Value.—When an alcohol or a hydroxylated fatty acid is boiled with acetic anhydride, the radical acetyl (C_2H_3O) replaces the hydrogen of the alcoholic hydroxyl. When such an acetylated compound is saponified, the acetic acid is re-formed and saturates a portion of the alkali. Thus if the acid and saponification values of such an acetylated fatty acid are determined in the ordinary way, the first should represent the combining power of the fatty acid, while the second is that of the fatty acid plus that of the acetic acid formed; and by deducting one from the other, an "acetyl value" is obtained similar to the ether value of an ordinary fat. Benedikt and Ulzer* applied this method as a means of measuring the hydroxyl groups present in the fatty acids; but it was shown by Lewkowitsch that most of the results obtained by their method are vitiated by the fact that anhydrides of the fatty acids themselves are formed in the process, and lead to a sort of "permanent saponification value."† He also pointed out‡ that true acetyl values were obtained by direct estimation of the acetic acid formed by distillation. He has recently shown that neutral fats could be acetylated similarly to fatty acids, and has devised a simplified method for determining their acetyl value, which he describes § as follows:—

"10 grm. of an oil or fat (or any other convenient number of grm.) are boiled with an equal volume of acetic anhydride for two hours in a round-bottomed flask attached to an inverted

* Monatsh. für Chem., viii. p. 40.

† Proc. Chem. Soc., 1890, p. 72; Journ. Soc. Chem. Ind., 1890, p. 660.

‡ Journ. Soc. Ch. Ind., p. 847.

§ Lewkowitsch, "Oils, Fats, and Waxes, p. 269, 3rd ed.; Cp. also Journ. Soc. Chem. Ind., 1897, p. 503.

condenser. The mixture is then transferred to a large beaker mixed with several hundred c.c. of water, and boiled for half an hour. A slow current of carbonic dioxide is conveniently passed into the liquor through a finely drawn out tube reaching nearly to the bottom of the beaker; this is done to prevent bumping. The mixture is then allowed to separate into two layers, the water is syphoned off, and the oily layer again boiled out in the same manner three successive times. The last trace of acetic acid is thus removed, as may be ascertained by testing with litmus paper. Prolonged washing beyond a certain limit causes slight dissociation of the acetyl product, which would lead to too low an acetyl value. The acetylated product is then filtered through a dry filter-paper in a drying oven to remove water.

The whole operation may be carried out quantitatively, and in that case the fatty matter is treated in a fashion similar to the *modus operandi* described for the determination of the Hehner value (p. 314); which is useful if it is desired to ascertain preliminarily whether a notable amount of glycerides of hydroxy acids be present in an unknown fat (p. 314).

About 5 grm. of the acetylated product are then saponified by boiling with alcoholic potash, as in the determination of the saponification value. If the "distillation process" be adopted, it is not necessary to work with an accurately measured quantity of standardised alcoholic potash. In case the "filtration process" be used, the alcoholic potash must be measured exactly. (It is advisable to use in either case a known volume of standard alkali, as one is then enabled to determine the saponification value of the acetylated oil or fat.) Next the alcohol is evaporated off and the soap dissolved in water. From this stage the determination is carried out either by (a) the distillation process, or (b) the filtration process.

(a) *Distillation Process.*—Add dilute sulphuric acid (1 : 10), more than is required to saturate the potash used, and distil the liquid in a current of steam. 600–700 c.c. of water are distilled off. As a rule this will be quite sufficient, and the last 100 c.c. will be found to require no more than 0.1 c.c. of decinormal alkali. Titrate the distillate with decinormal potash, using phenolphthalein as an indicator, multiply the number of c.c. by 5.61, and divide by the weight of substance taken. This gives the acetyl value.

(b) *Filtration Process*.—Add to the soap solution a quantity of standardised sulphuric acid exactly corresponding to the amount of alcoholic potash employed and warm gently, whereupon the fatty acids will readily collect on the top as an oily layer. (If the saponification value has been determined, it is of course necessary to take into account the volume of acid used for titrating back the excess of potash.) Filter off the liberated acids, wash with boiling water until the washings are no longer acid, and titrate the filtrate with decinormal alkali. The acetyl value is calculated in the manner shown above (a).

Both methods give identical results; the latter requires less time, and will therefore be found more convenient.

The distilled water used in determining the value by either the distillation or filtration process should be carefully freed from carbonic acid by previous boiling, or otherwise serious errors may result. Even the water used for generating steam in the distillation process should be brought into violent ebullition before the steam is passed into the distilling flask. This source of error may easily creep in in the case of very hard water. Check experiments with pure acetic acid will readily guide the operator. In order to facilitate the separation of insoluble fatty acids in the filtration process, it will be found useful to add a slight excess of mineral acid. Of course this amount must be measured accurately and deducted from the alkali required for determining the dissolved acids.

The acetyl value of the free fatty acids may be determined accurately by acetylising as above described, and estimating the acetic acid by the distillation process, but for reasons already given, the filtration process is not applicable.

The *acetyl value* determined as described is the number of milligrams of potassium hydrate required for the neutralisation of the acetic acid obtained by saponification of 1 gm. of the acetylated product (not of the original fat).

Acetylation is a general chemical method for the determination of alcoholic hydroxyls. It is not affected by the acid hydroxyl of the carboxyl group, hence in hydroxy acids it measures the hydroxyls attached to the hydrocarbon chain, and unhydroxylated acids have no acetyl value. Similarly, a glyceride, in which all the hydroxyls of the glycerin are replaced by the radicals of unhydroxylated fatty acids, has no acetyl value, but

free glycerin has all its three alcoholic hydroxyls replaced by acetyl, forming triacetin, the simplest fat; and mono- and diglycerides, in which only 1 or 2 of the hydroxyls are replaced by fatty acids, take up 2 or 1 acetyl groups respectively. Alcohols such as cholesterol, phylosterol and the wax alcohols also take up acetyl groups replacing their alcoholic hydroxyls. The meaning of the acetyl value is thus often very complicated, and it is only in the case of free hydroxy acids or their neutral glycerides, or of free alcohols, that its indications are unambiguous. In the case of fats, it may merely indicate the amount of free or partially free glycerine, and thus simply measure the rancidity. In this case, the acetyl value of the free fatty acids, if any, would be included. Where natural or rancid fats contain volatile or soluble acids, these will be reckoned as acetic, and hence raise the apparent acetyl value. Hence, to obtain true values, these acids must be determined in a similar way on the unacetylated fat, and deducted from the acetyl values found.

Thus the exact conclusions to be drawn from the acetyl value are usually, to some extent, a matter of conjecture, and it would be obviously useless to give detailed tables, but a few of the more important values are given in the tables of constants, pp. 349-350. For further information, the reader may be referred to Lewkowitsch as already cited. It is probable that the method, if applied to the study of oxidised oils, in conjunction with their fall in iodine value, and the oxidised acids separated by their insolubility in petroleum ether (p. 314), would give interesting information as to the nature of the oxidation products, which are evidently not simply hydroxy acids. This has, to a certain extent, been attempted by Ruhsam in his examination of *dégras* (p. 337); but as he used Benedikt and Ulzer's original method, his numbers will require confirmation.

D. SPECIAL APPLICATIONS OF FAT ANALYSIS.

Tallow.—This is the fat of domestic animals, principally ox and sheep, but sometimes goat. It consists mainly of glycerides (either simple or "mixed") of oleic, stearic and palmitic acids. "Rendered tallow" includes fat from all parts of the carcass; while "pressed tallow" or "oleostearine" is the harder residue from beef suet (kidney and bowel fat), of which the softer part is

used in the manufacture of margarine. Mutton tallow is generally harder and whiter than beef. Tallow should be white or yellowish, with only a slight characteristic smell. Goat, and, in a less degree, mutton tallows may be recognised by their odour; and adulteration with distilled stearine from recovered fats, or with the cheaper waste greases from glue works and tanneries, is often similarly indicated. Tallow should melt at a temperature not much below 40° C. for beef, and 45° C. for mutton tallow, to a transparent colourless or slightly yellow liquid, containing at most traces of water. The solidification temperature is several degrees lower. (The free fatty acids usually solidify at 40° – 45° C., though very soft samples may be a degree or two lower (p. 350). The solidification temperature is mainly dependent on the proportion of oleic to stearic and palmitic acids.) Paraffin wax is sometimes added to raise the melting point.

The melting and solidifying points of tallow, and especially of its free acids, afford much information as to its hardness and quality for candle-making, but little as to its purity from adulteration.

If tallow contains solid matter, or forms a turbid fluid on melting, moisture should be determined, of which it should not contain more than a mere trace; and if still turbid after drying, it should be filtered and the filter extracted with ether or petroleum ether, as described on p. 285, and the nature of the solid impurities determined. Lime is sometimes added to tallow, to thicken it and enable it to retain more water, and in this case will remain on the filter as lime soap, and may be determined after ignition. Fragments of animal tissue, and traces of lime phosphate, may be present as accidental impurities. Boiled with water, tallow should give up no free acid which would redden lacmoid paper, or methyl orange (presence of free mineral acids).

Physical constants (Table, p. 350) should be determined in the clear filtered fat, to which it is best not to add the portion extracted from the filter by solvents. The specific gravity is best determined at 100° C. (p. 291), and should be about 0.860, mutton tallow being sometimes slightly lower and beef higher than this figure. A higher gravity might indicate the presence of rosin, which in many cases is also betrayed by its characteristic taste and smell. For its detection and estimation, see p. 316. Cotton seed stearine (p. 327) also somewhat raises the gravity of tallow,

while it is lowered by "distilled stearine" (p. 329), and still more by paraffin wax, which at the same time raises its refractive index and lowers its saponification value, and may be determined as "unsaponifiable matter." Cotton seed stearine (and fish stearine also) would raise the iodine value on account of the oxidisable fats they contain.

The saponification value of tallow is about 196; it would be raised by the presence of palmitic, or cocoanut oil, or by acid products of rancidity or oxidation, and lowered by the presence of waxes and unsaponifiable matter.

The acid value of good tallow should be low, but in rancid tallows may reach 15. Higher numbers indicate adulteration with free stearic acid (distilled stearines, p. 329).

The iodine value of tallow varies according to its hardness and consequent percentage of olein, from about 35 to 45; and in absence of adulteration the percentage of oleic acid may be calculated from it (see pp. 303, 306). It is stated, however, that tallow may naturally contain traces of less saturated acids than oleic, perhaps derived from oil-cake feeding. A lower iodine value than 35 would indicate the presence of palmitic or cocoanut oils, of wool-fat, or of paraffins; while a higher than 45 points to adulteration with drying or semi-drying oils, or with rosin.

Distilled or wool grease stearine (p. 329) would be indicated by lowered refractive index, high acid value, peculiar and characteristic smell, and the presence of cholesterol and isocholesterol among the unsaponifiable matter (see p. 313).

Beside actual tallow, other animal greases are more or less used in leather manufacture which differ from it chemically in containing a larger proportion of olein in relation to the stearin and palmitin, and which are consequently softer, and of lower melting point.* Horse fat, and especially the soft grease of the neck (*Kammfett*), the grease obtained in glue boiling from the fleshings of the hides of cattle and other skins, the grease pressed out of sheep skins, and bone fat obtained by boiling bones, all belong to this category, to which lard may also be counted. If these greases are appropriately cooled and pressed either in a

* Probably some of the characteristics of animal fats are due to their "mixed glycerides," as well as to the total quantities of the three acids which they contain. A "mixed glyceride" is one in which two or even three different fatty acids are combined with one molecule of glycerin.

solid state in the hydraulic press, or, more conveniently, in a semi-liquid condition by means of the filter press, a harder tallow may be separated from an oil which does not seem to differ chemically from the much more costly "neatsfoot oil" obtained by boiling the feet of cattle, and sometimes of sheep and horses. The oils and greases are often nearly white, but sometimes dark-coloured from the action of putrefying animal matter or of heat, but this coloration, unless very dark, would not interfere with their use in leather manufacture, and they are perfectly suitable for use as stuffing greases, and mostly so low in price as to be much less liable to adulteration than the more expensive oils and fats for which they might be substituted.

Apart from the question of colour, the analysis of these fats is similar to that of tallow. As, no other unsaturated acid is likely to be present in material quantity, the percentage of oleic acid may be calculated from the iodine value, which for pure olein is 86.2, and for oleic acid 90.07. The titer test (p. 294) will also give information. The acid value will vary according to the mode of manufacture. Grease obtained from limed hide or skin by boiling or pressure, without the use of acid to decompose the lime soap, is often nearly neutral; while if acid has been used, the amount of free fatty acid value may be considerable. This is very injurious if the fats are to be used as lubricants, but of no consequence for stuffing greases, so long as mineral acids are absent. These fats, containing no unsaturated acids but oleic, are not likely to "spue," or "gum," but may cause a white efflorescence of crystalline fatty acids.

The saponification value should be practically the same as that of tallow and neatsfoot oil, i.e. about 195. Pure olein has a saponification value of 190.4, stearin of 189.1, and palmitin of 208.8, while the saponification or acid value of free oleic acid is 198.6, of stearic 197.1, and of palmitic 218.7. In the case of mixtures of the three acids only, it is easy to infer the approximate percentage of palmitic acid from the saponification value of the fats or mean molecular weight of the acids only,* and

* Thus, supposing a pure neutral tallow to have a saponification value of 196, and taking the combined value of the olein and stearin at 190, we have an excess value for palmitin of 6, while the difference for 100 per cent. should be 19.7 and by rule of three we obtain 30.5 per cent. of palmitin. If the iodine value of the tallow is 40 and of pure olein 86.2, we similarly obtain 46.4 per cent. of olein, and taking this into account, 32.0 per cent. of palmitin and 21.6 per cent. of stearin.

still more exactly if the percentage of oleic acid as calculated from the iodine value is taken into account.

The specific gravity of the softer fats at 105° C. is practically the same as that of tallow, viz. about 0.860, but their refractive index is somewhat higher from the larger percentage of oleic acid.

Neatsfoot Oil.—This oil is considerably employed in calf-kid dressing, and as it does not differ chemically from the oils obtained by pressing the soft fats already mentioned, it will be convenient to speak of it in this connection. Its specific gravity is .914–.916 at 15° C., that of tallow and lard oils being a little lower. Sperm and bottlenose ("arctic sperm") oils, and wool grease oleine and mineral oils are the only oils of materially lower specific gravity, and are easily recognised by the presence of unsaponifiable matter, though of course the price* of the first two precludes their use in adulteration. The same may be said of olive oil, which is identical in density, and in most of its physical and chemical constants, but rape oil and cotton-seed oil might at times be used as adulterants. Cotton-seed oil would raise the iodine value, and specific temperature reaction, but would not much alter the saponification value. Rape would lower the saponification value, and raise the iodine value and specific temperature reaction, but from its price is not so likely to be present. The iodine value of neatsfoot is generally about 70, as it contains considerable percentage of stearin and palmitin. This will vary much with the temperature at which the oil has been filtered, which in "cold tested" oils is often a low one. If neatsfoot, lard, tallow and olive oils contain no unsaturated acid but oleic, their iodine value cannot exceed 86, the iodine value of pure olein; but Lewkowitsch states that the iodine value of American lard oils sometimes reaches 106. As regards olive oils see below. It is difficult to say in these cases how far the differences are due to adulteration, and how far to actual variation in the oils produced by differences of climate or nourishment. Most of the seed oils contain less saturated acids such as linolic, and therefore have higher iodine values; thus that of rape is 101, and of cotton seed 108. The specific temperature reaction with

* The relative prices of oils are often very valuable in determining probable adulterants, though occasionally a more expensive oil may be added in small quantity to improve the appearance or adjust constants.

sulphuric acid (p. 299) affords a still more rapid and equally decisive test, both for neatsfoot and other tallow oils, and for olive oil. . . . The specific temperature does not exceed 90–94° C. for any of these, while for rape it is 125–155° C., and for cotton-seed 168–170° C. The saponification value for olive, neatsfoot, and tallow oils is about 193; and if lower, the probable cause is addition of mineral oil, though rape oil with a saponification value of 177 would lower it if added in considerable quantity.

Olive Oil.—From what has just been said, it will be seen that olive oil considerably resembles tallow and lard oils, but its adulteration with oils of this class can usually be detected by taste or smell. Its principal difference consists in its containing no stearic acid, and in its larger proportion of olein to solid glycerides, as compared to the 'non-drying animal oils pressed at ordinary temperatures, which contain considerable amounts of dissolved "stearine," which separates and renders the oil turbid or semisolid when exposed to low temperatures. Such oils are technically called "tender." By racking or filtering these oils near the freezing point, even this difference is removed or diminished.

From its higher percentage of oleic, and the presence of small quantities of less saturated acids, olive oil does not become turbid till near freezing, and its fatty acids have a lower solidification point. Their solidifying point (p. 292) ranges, according to Lewkowitsch, from about 17° C. for the finest oils to 26° C. for Gallipoli. From the same cause it possesses a higher iodine value than the animal oils, ranging from 79 up to 86, the theoretical limit for pure olein. It has even been stated to exceed this figure, but more frequently the high iodine value is due to adulteration with refined cotton-seed oil, which of course raises the iodine value. Arachis, colza (rape) and sesame oils are also frequent adulterants, and may mostly be detected by their raising the specific temperature reaction and to a lesser extent, the iodine value. Mineral oils are sometimes added. They lower the saponification and iodine values, and may be determined as unsaponifiables. In mixture with other oils, they are made to serve for adjusting the constants to those of a normal olive oil. For more detailed particulars of the examination of olive oil, the reader is referred to Benedikt and Lewkowitsch's 'Oils, Fats and Waxes,' or to Allen's 'Com-

mercial *Organic Analysis*, vol. ii. Olive oils which have an acid value exceeding 10 are said to be unsuitable either for lubrication or burning, but may be purified by washing with sodium carbonate solution.

Besides these natural fats, the dissolved fats which separate as "foots" from many oils in cold weather are frequently filtered out, and sold as greases. They are often contaminated with albuminoid and other impurities precipitated or settled out of the oil, and are usually called "stearines," but must not be confounded with the "distilled stearines" (p. 329), which consist mainly of free fatty acids. These foots, if dark or too impure for use, are frequently themselves distilled, yielding free fatty acids and hydrocarbons (like "Yorkshire grease"), from which distilled stearines are prepared by pressure which much resemble the ordinary "distilled grease stearine," but of course without the peculiar products of wool-fat which are characteristic of the latter.

Fish Fat or *Fish Stearine* settles out of fish oils when exposed to cold, and is used in currying and for mixture with dégras. It consists mainly of the glycerides of the solid acids, mixed with considerable quantities of the fish oil. Lewkowitsch has found its iodine value as high as 104, and higher values have been recorded, so that it must contain unsaturated solid fats.

Cotton-Seed Stearine is a similar product from cotton-seed oil. Both these fats may be recognised in tallows and other fats naturally containing only olein in mixture with stearin and palmitin by the higher iodine value and specific heat reaction due to their less saturated acids.

Recovered Wool-fat, "*Yorkshire Grease*."—Raw wool contains in addition to organic potash salts, considerable quantities of a peculiar grease derived from the sweat and sebaceous glands. In its pure form it contains no glycerides, but consists mainly of waxes, or ethers of fatty acids with alcohols of high molecular weight, together with uncombined alcohols of the same type, and among others of cholesterol and isocholesterol. It is of yellow colour, faint smell and salve-like consistence, and possesses the property of easily emulsifying with water, which renders it very valuable both in leather manufacture and as an ointment. "*Lanoline*" is a mixture of purified wool-fat with about 22 per cent. of water.

It is usually removed from the wool by washing with solutions of sodium carbonate and soaps, and the soapy liquors so obtained are decomposed by addition of sulphuric acid. The "magma" of fatty acids is filtered off, dried and subsequently pressed in a steam heated press. The grease thus obtained is known as "Yorkshire grease" or "recovered grease."

Yorkshire grease is a yellowish-brown fat of salve-like consistence, and unpleasant and characteristic smell. It contains, in addition to pure wool-fat, the free fatty acids derived from the soap used in washing, and occasionally mineral oil, if this has been contained in the wool oils used in manufacture. Only a portion of its ethers or waxes can be saponified by the ordinary method of boiling with alcoholic potash, but complete saponification may be effected by heating with double-normal alcoholic potash under pressure at 105° – 110° C. in a strong glass or copper flask in an oil or salt solution bath. Schmütz-Dumont * gives the partial saponification value of pure neutral wool-fat as obtained by boiling in the usual way at atmospheric pressure as 84–86, which was hardly increased by prolonged boiling. According to Lewkowitsch † the value on complete saponification under pressure is about 102. Complete saponification may also be obtained by the use of sodium ethoxide, or by adding small pieces of metallic sodium to the fat while boiling with absolute alcohol. About 5 grm. sodium to 100 c.c. absolute alcohol is a suitable quantity ‡ (cp. p. 310).

According to Lewkowitsch § the percentage of fatty acids in pure wool-fat is about 60, and their mean molecular weight 327, with a melting-point of 41.8 and an iodine value of 17. The iodine value of purified wool-fat itself is stated by the same author as varying from 17 to 29, possibly because of impurities. The percentage of unsaponifiable matter (alcohols) is about 44. It is best shaken out with ordinary ethyl ether, in which it is more soluble than in petroleum ether.

The complete analysis of recovered grease is extremely difficult, and readers may be referred to the work of Lewkowitsch. ||

* Ding. Polyt. Journ., 1895, ccxcvi. p. 234.

† Oils, Fats and Waxes, p. 528.

‡ Kossel and Obermüller, Zeits. f. Physiol. Chem., xv. pp. 321–330. D. R. Pat. 55,057.

§ Oils, Fats and Waxes, p. 528.

|| Journ. Soc. Chem. Ind., 1892, p. 134.

There is, however, no particular difficulty in determining the ordinary constants, except such as arises from the difficult saponification of the waxes, and their tendency to form persistent emulsions with the solvents.

In the United States recovered wool-fat or "Yorkshire grease" is known under the name of "English dégras," and is much used for currying. It is needless to say that it differs totally in its composition from real dégras, but in common with it it possesses the quality of easy emulsification with water and freedom from rancidity, and is therefore a valuable fat for the currier. "Holden fat" or "dégras" consists of a similar product mixed with fish oil, and, as has been already stated, wool-fat is much used to mix with genuine dégras.

Recovered grease is frequently purified by distillation in a current of superheated steam. Much of the free fatty acids, and a portion of the alcohols and neutral waxes distil over unchanged, but a considerable part of both is broken up into volatile hydrocarbons which do not differ chemically from those of petroleum oil, and like them are usually fluorescent. The distillate is usually separated by cooling, crystallising and pressing into a liquid portion or "oleine" and a solid "stearine." The former contains most of the hydrocarbon oils, together with liquid fatty acids; while the latter consists mainly of free stearic, palmitic and isooleic acids. The "oleine" is used principally as a "wool oil," but from its low price might sometimes be employed for adulterating common cod oils. The "stearine" forms a very valuable stuffing grease, which in England to a large extent takes the place of the oleostearine used in the United States.

Distilled Grease Stearine is a solid fat varying in colour from nearly white to yellowish brown, and in hardness and solidifying point with the conditions of the pressing. Lewkowitsch points out that it may be distinguished from commercial stearic acid from other sources by the absence of marked crystalline structure, by its high iodine value due to the presence of isooleic acid, and by its strong isocholesterol reaction (p. 313). Its odour is also persistent and characteristic. It is distinguished from tallow by its high acid value, and the absence of glycerides, as well as by the above characteristics. It is also marked by its lower gravity, about 0.806 at 100° C., and its lower refractive index.

The method of analysis usually adopted with distilled stearines is to saponify in the usual way, using 50 c.c. of N/2 alcoholic potash for 3-4 grm. of fat, and boiling at atmospheric pressure. After determining the saponification value by titrating back with N/2 hydrochloric acid, the solution is treated with a pinch of sodium carbonate to neutralise the possible minute excess of acid due to the titration, and shaken out with petroleum or ethyl ether, great care being taken, by avoiding violent shaking till most of the soap is removed, to prevent the formation of persistent emulsions. In obstinate cases, patience and the addition of alcohol to the wash water will generally enable a separation to be effected.

For commercial purposes it is often calculated that each c.c. of normal alkali consumed corresponds to 0.284 grm. of stearic acid, no notice being taken of the slightly different molecular weights of other acids present, nor of the possible presence of lactones and traces of neutral fat on the one hand, or of the small quantities of waxes present on the other, parts of which escape complete saponification.

If the acid value and the saponification value of the separated free fatty acids be determined, the presence of lactones (p. 317) will be shown by the excess of the latter, and can be calculated as stearylactone from the difference, each c.c. of N/1 potash corresponding to 282 mgr. The saponification value of stearylactone is consequently 198.9. Great care must be taken in the preparation of the fatty acids for the determination of lactones that all saponifiable matter is completely saponified, or at least thoroughly removed from the soap solution by shaking out. For this purpose ethyl ether is preferable to petroleum ether in the case of wool-fat and fish oils containing liquid waxes, since the higher alcohols of which the unsaponifiables consist are not readily or completely removed by the latter solvent. In case unsaponified waxes remain mixed with the fatty acids, the molecular weight as determined from the acid number will appear abnormally high, and if any further saponification takes place in determining the saponification value an apparent "permanent saponification value" will result.

Cod Oil.—Genuine cod oil is obtained from the liver of *Gadus morrhua*, the common cod, and contains a large proportion of very unsaturated and oxidisable fatty acids. Möller's "Hy-

droxyl-free" oil, is rendered in an atmosphere of carbonic acid, to prevent oxidation, and reaches an iodine value of 165, but the ordinary commercial oils contain oxidised acids and have iodine values of about 155. On oxidation by blowing or exposure to air, the gravity and viscosity of the oil increases largely (s.gr. up to 1.0812), and the iodine value correspondingly falls, and the oil becomes partially insoluble in petroleum ether and the ordinary oil solvents.* The pale medical oil is obtained by steaming the perfectly fresh livers. The brown oil used in leather manufacture is usually prepared from livers more or less putrid, or from a second steaming of the fresh livers, or sometimes, by allowing the livers to putrefy, collecting the oil which runs out, and rendering the residue by fire heat. Such oils are made in Newfoundland and Norway, the former being most esteemed by curriers, possibly because it is rendered at a higher temperature, which, by precipitating albuminous matters, lessens its tendency to "spue," or exude in an oxidised form on the surface of the leather. This troublesome defect is apparently due to some kind of fermentative change, and is favoured by the presence of nitrogenous matter, the drying tendency of the oil, and probably by bacterial fermentations in the leather itself. It is said to be most frequent with oils of a high acid value, either from the greater oxidisability of the free fatty acids, or, more probably, because the acidity is, itself, an indication of rancidity and a tendency to change. Spueing is much favoured by the presence of iron salts, and other oxygen-carriers, and hence is particularly common on iron-blackened leathers.

"Coast Cod" oil is a liver oil obtained in this country from cod livers mixed with those of various other fish, such as ling, haddock and hake, several of which are of higher iodine value, and consequently more oxidisable than genuine cod,† and is frequently very badly manufactured. It varies much in quality.

Among the investigations of the unsaturated acids of marine oils, those of Fabron (Chem. Zeit., 1893, p. 684; Abst. Journ. Soc. Ch. Ind., 1893, p. 935), Bu'li (Chem. Zeit., 1899, p. 996; Abst. Journ. Soc. Ch. Ind., 1900, pp. 73 and 176), and Heyerdahl (Moller's "Cod-liver Oil and Chemistry," London, 1895, p. 89), may be particularly mentioned, but further investigation and confirmation are much needed. It is doubtful if true oleic acid is contained in any of these fish oils.

† Compare Procter and Holmes, Journ. Soc. Ch. Ind., 1905, p. 1287; and Procter and Bennett, *ibid.*, 1906, p. 798, who give a method of determining the bromine value of the more unsaturated acids yielding hexa- and higher bromides.

the best being probably equal to Newfoundland oil, but on the whole it has a low reputation. It is frequently mixed with oils from other fish refuse, damaged herrings, and so forth; and is beside very liable to be adulterated with mineral oils.

The principal adulterants of cod oil are mineral oils of high gravity, rosin oils, other fish oils, and occasionally cotton-seed and other seed oils, when the price will allow. A higher priced oil may sometimes be used in mixture as an adulterant when its lighter colour makes the mixture more saleable, or in order to make the oil answer to the ordinary tests.

The most important determination is generally the saponification value, which should be about 184. Anything much lower than this indicates adulteration with mineral or rosin oil, or possibly with distilled "oleine" or shark-liver oil. These may be detected by shaking out unsaponifiable matter (p. 309). If shark or dog-fish liver oils are suspected, ethyl ether should be used for shaking out. The saponification value of shark oil is about 160, and it contains up to 10 per cent. of unsaponifiables due to the presence of liquid waxes. Other marine oils containing liquid waxes are too expensive to be used as adulterants. "Distilled oleine" is the liquid portion of the distillation of recovered grease (see Wool-fat, p. 327), and consists mainly of free oleic acid and liquid unsaponifiable hydrocarbons. It is mainly used for "wool oil," but from its cheapness might be employed as an adulterant. It would be indicated by the presence of unsaponifiables in conjunction with a high "acid value." Distilled oleine has an acid value of 110 or more, and a total saponification value of 120-150.

A high saponification value is generally due to advanced oxidation of the oil leading to the formation of acids of lower molecular weight. This is accompanied by the formation of oxidised acids insoluble in petroleum ether, a rise in the gravity, refractive index, and specific temperature reaction, and a lowering of the iodine value. Similar effects are also produced by addition of oxidised ("blown") cotton-seed or seal oil. Oils are frequently blown to a moderate extent in order to bleach and deodorise them. The amount of oxidation is best determined by separating the resinoid oxidised acids insoluble in petroleum ether ("dégras-formers") p. 314.

The gravity and refractive index of pure cod oils are both

high, the former being about 0·926–30, and the latter 1·4800–50 at 15° C. High refractive index with normal or low gravity often indicates the presence of mineral oil. Where both are high, rosin oil or considerable oxidation are indicated.

Where mineral or rosin oil is suspected, the unsaponifiables should be separated according to p. 309. In ordinary cases light petroleum spirit is the best solvent, but where it is desired to separate the higher alcohols, naturally present in shark liver and some other marine oils, ordinary ethyl ether must be employed.

The "acid value" is of importance, not because the presence of a little free acid is injurious to leather in itself, but because it usually indicates a tendency in the oil to become rancid (or possibly its adulteration with "oleine"). Oils with high acid value are said to be unsuitable for chamoising, and to have a greater tendency to "spue." Mackay has shown that free fatty acids oxidise more rapidly than neutral oils.*

The "iodine value" of a pure medical cod-liver oil seems to be about 158, but that of the genuine brown cod is usually lower, being reduced by oxidation. It would also be lowered by the presence of mineral or rosin oils, or of any of the non-drying or semi-drying oils, of which cotton-seed, with an iodine value of about 106, is perhaps the most likely to be used as an adulterant. Linseed oil is almost the only oil which has a higher iodine value than cod, and is itself surpassed in this respect by skate and haddock liver oils, which are frequently present in "coast-cod."

There are as yet no chemical methods by which admixtures of other marine oils with cod can be certainly detected, except in the case of such oils as shark liver and some whale oils, which contain liquid waxes, and hence unsaponifiable matter. Sometimes taste or smell may assist. The many colour-reactions which have been described are of little value. If a drop of concentrated sulphuric acid be added to cod-liver oil on a watch glass, it will form a violet spot, often with red or violet rays. This reaction is given still more strongly by shark oil, and is common to all fresh liver oils, but when old and rancid, only a dirty reddish-brown is obtained. If, instead of adding the acid direct to the oil, about one drop of the latter is dissolved in a cubic centimeter of carbon disulphide and a drop of sulphuric acid added, a beautiful violet colour is developed, changing slowly

*Journ. Soc. Chem. Ind., 1894, p. 1164; 1895, p. 940; 1896, p. 90.

to red and brown. Old oils only give the red coloration (which is also given by palm oil), and not the violet. These colour reactions are due to the presence of lipochromes and cholesterol. Similar results are obtained by using chloroform as a solvent as in the cholesterol reaction described on p. 313. Rosin and rosin oil also give red coloration with sulphuric acid. . . . These reactions might be valuable for the detection of liver oils in other oils, but are useless where liver oil is known to be the principal constituent. Mineral and rosin oils render oils containing them quite unsuitable for chamoising, but are not injurious to tanned leather, and in many cases principally objectionable on account of their lesser pecuniary value.

Although other marine oils than cod are little used in England for leather manufacture except as adulterants of cod oil, they are considerably employed on the Continent, and apparently with advantage, and these pages would not be complete without a short notice of them, and a few words must also be said on the hydrocarbons which are used as adulterants, and occasionally as intentional additions to stuffing greases or for oiling off levants.

Other Fish-Liver Oils.—It has been mentioned that in "coast-cod" the oil extracted from the livers of other fish is generally included. Of these fish the principal are the ling (*Molva vulgaris*), haddock (*Merluccius aeglefinus*), coal-fish* (*Gadus merlangus*), and hake (*Merluccius communis*), and not unfrequently that of the Arctic shark† (*Somniosus microcephalus*), and of the dog fish (*Scyllium canicula* and *catalus*), which also belongs to the shark family. Some constants of these oils will be found on p. 349. Shark and dog-fish liver oils contain considerable quantities of unsaponifiable liquid waxes analogous to those of sperm and dolphin oils. This lowers the saponification value, that of shark oil being about 160, and its iodine value is also low, being about 115. The unsaponifiable alcohols of the waxes are not easily shaken out with petroleum spirit, but by shaking with ordinary ether, about 10 per cent. may be removed from shark oil. Exact constants are not available for dog-fish oil, but it is probably closely similar to that of the Arctic shark. Boegh and Thorsen‡ give a method of recognising shark-liver oil through

* Sometimes called "Black Jack"; German and Norse, *Sai* or *Sei*; Fr. *Merlan*.

† Formerly *Scymus microcephalus*, or *borealis* or *Lamargus borealis*, the "basking" shark, Norse *Baakjarring*; Danish, *Bævkål*; Ger. *Luskal*.

‡ Collegium, 1904, p. 73.

the greater insolubility of its soap in hot water, which is no doubt due to the presence of the liquid waxes alluded to. Their process consists in saponifying 10 grams of the oil in a flask with 50 c.c. of alcohol and 10 c.c. of a solution of pure sodium hydrate, containing by titration approximately 0.36 gm. of sodium hydrate per cubic centimeter. The operation is carried out on the water-bath, if necessary with a reflux condenser, and the solution is finally evaporated to dryness. 50 c.c. of boiling distilled water is then added, while the flask is heated on the water-bath, and frequently shaken, and successive additions of 5 c.c. of distilled water are made until the soap forms a perfectly clear liquid, or no further solution takes place. The total quantity of water used is noted, and if it exceeds 70 c.c., it may be assumed that shark oil is present. Shark oil alone will not give a clear solution, and a mixture of equal parts of this and cod or coal-fish liver oils requires over 200 c.c. of boiling water to do so. It is probable that similar results would be obtained with mixtures of other oils containing liquid waxes, but most of these are too expensive to be used as adulterants of ordinary fish oils. Shark liver oil is said to be particularly prone to cause the resinous exudation on leather known as "spueing," and from its large percentage of unsaponifiables is quite unsuitable for chamoising.

The other liver oils named are very similar to cod in their general characteristics. Skate liver oil and haddock oil seem to be remarkable for high iodine values, a sample of the former repeatedly examined in the author's laboratory having an iodine value of 187. It is not known whether these oils are in any way less suitable than that of cod for purposes of leather dressing, but some differences in their rate of oxidation were observed by Messrs. Procter and Holmes in their experiments on "oil oxidation."^{*}

Fish Oils.—Under this head may be classed all those oils which are extracted, not from the liver, but from the body or intestines of several fish. Lewkowitsch points out that those fish (e.g. cod) which have very oily livers, rarely have much oil in other parts of the body, while in many others, the largest yield is from the body and intestines. The principal fish oils are menhaden, porgie, or "Straits" oil from *Alosa menhaden*, a fish somewhat larger than a herring, which is caught in large

quantities off the New England coast; sardine oil, which is obtained in the preparation of sardines for food; Japanese sardine oil or Japanese fish oil, which is extracted from the sardine, either by boiling or by allowing it to rot in heaps, and subsequently pressing the mass; herring oil, of which considerable quantities are occasionally made in England from damaged herrings, and which is generally mixed with other fish oil from the refuse of various fish, and not unfrequently added to "coast cod." Most of these oils are very similar in their chemical characteristics to genuine cod oil, but from their mixed character and uncertain origin no very definite constants can be given. The specific temperature reaction of menhaden oil is very high, and is given by Thomson and Ballantyne as 306. Its drying power is so considerable that it is sometimes used as a paint oil for outside work, and it is probable that leather curried with it would be particularly liable to "spue." It is frequently used for adulterating Newfoundland cod. It is quite suitable for oiling sole leather in warm weather, but gives trouble in cold from its high percentage of solid acids, which might no doubt be removed by filtration at a lower temperature. The saponification values of these fish oils are generally higher than that of unoxidised cod oil, averaging about 190. Sardine oils may often be detected by their taste and smell of sardines, but appear to lose it on oxidation by exposure to the air.

Whale Oil.—This is extracted from the blubber of various species of whale of the genus *Balæna* and *Balænoptera*; and varies considerably in quality, not only according to the species but the method of extraction, Nos. 0 and 1, steam-boiled at low temperatures, being pale in colour, with little fishy odour, and almost neutral, while 3 and 4 extracted under pressure and often after some putrefaction are darker and of more fishy smell, and with high acid values (25–100). The "foots" contain much palmitin, and the oil contains olein and semi-drying oils like fish oils, but its chemical constitution has been little investigated, and probably varies considerably with the species from which it is obtained. It sometimes contains traces of spermaceti, but the total unsaponifiables do not exceed 2 or 3 per cent. Its saponification value is 188 or a little over. Its iodine value and specific temperature reaction seem to vary considerably. It is much used on the Continent for chamoising, and consequently is one

of the constituents of dégras. It is probably perfectly suitable for use in currying.

Seal Oil.—Extracted from the blubber of various species of seal (*Phoca vitulina*, *A. grænlandica*, *P. lagura*, *P. Caspica*). It is frequently mixed with fish oils, as in the Swedish "Dreikronenthran" (Three Crown Oil). It considerably resembles both whale and fish oils, and cannot be detected in mixture with these by any of the ordinary analytical reactions. Its saponification value seems generally to be about 192, though it sometimes falls as low as 185 in reputed pure samples. . . . Its iodine value is high, generally ranging from 125 to 160, and its specific temperature reaction 212–229, according to Thomson and Ballantyne. As the specific temperature reaction of cod oil is considerably higher, this may afford a means of inferring the presence of seal oil in mixtures. Seal oil itself is rarely adulterated, except with rosin or mineral oils which may be detected as unsaponifiables; of which the pure oil usually contains only about $\frac{1}{2}$ per cent. It is used largely on the Continent for chamoising and currying, and seems quite suitable for these purposes, especially in mixture with the more oxidisable oils such as cod and menhaden, of which it moderates the oxidation.

Dégras and Sod-Oil.—Genuine dégras is the residual oil wrung or pressed out of chamois-leather in the French method of manufacture, in which the skins are fulled with whale, seal, fish, or cod oil; or a mixture of these, and oxidised by exposure to the air in warm rooms. A portion of the oxidation products are fixed in the leather, and together with the acrylaldehyde evolved produce an oil tannage, while the unoxidised products, and a considerable proportion of oxidised acids referred to on p. 314 are pressed out after dipping the skins in hot water. In some cases skins are worked over and over again merely for the production of dégras, which may therefore be regarded as essentially an oxidation product of marine oils. In fact, a good deal of artificial dégras is now manufactured by "blowing" or directly oxidising the oil under suitable conditions; and apparently is equally suitable for currying. In the genuine manufac-

Interesting work on dégras has been published, among others, by Eitner, *Der Gerber* 1890, 85 *et seq.*; 1893, 245, 255; Simand, *ibid.*, 1890, 243 *et seq.*; Ruhsam, *Ding. Polyt. Jour.*, 1893, 285, 233; Fahrion, *Zeits. für angew. Chem.*, 1891, 172; 1893, 146; *Chem. Zeit.*, 1893, 434 and 684; *Deutsche Gerber Zeit.*, 1892, 33 *et seq.*

ture, the oil from the first wringing or pressing is called "*première torse*," and all the oil actually recovered from the skins is "*moëllon*." Its value to the currier consists in its ready miscibility and emulsification with water, of which genuine *dégras* invariably contains from 10 to 20 or even 30 per cent. This leads to its very complete distribution in a finely divided condition on the leather fibre, which gives softness without a greasy feel. The oxidised fatty acids ("*dégras-former*") are also said to be important as producing a sort of retanning effect. For methods of determination, see p. 314.

Sod-oil formerly differed from *dégras*, because, in the earlier English methods of chamois manufacture, the skins are allowed to heat in pile, and a more intense oxidation is thus obtained, with so much thickening of the oil that it can no longer be removed by pressing, but must be washed out with an alkaline lye, from which it is separated by addition of sulphuric acid. It is thus liable to contain, beside much water, considerable traces of acid, or of alkaline soap, or even of both in imperfect mixture. "It is frequently purified and deprived of water by heating in a steam pan, when the water is either evaporated or settles to the bottom with many of the other impurities. Such an oil is useful as a constituent for currying greases, but it is no substitute for the genuine *dégras* for the special purposes for which the latter is employed.

Now, however, many English chamoisers treat their goods very similarly to the French, and remove a large part of the oil by pressing only, and there seems no reason why such oils should be inferior to the best French *dégras*. As much of their value depends on their emulsion with water, it is a mistake to "evaporate" such sod-oils.

The pure *moëllon* is never sold unmixed, but always receives additions of untreated oils, and usually of tallow, which must hardly be regarded as adulterants. More questionable but frequent admixtures are wool-fat or recovered grease, and mineral oils.

From what has been said, it will be seen that the analysis of, so complicated a mixture as a commercial *dégras* presents no common difficulty, and that a complete determination of its various constituents is generally impossible.

Estimation of water is always important. This may be done as in the case of egg yolk, p. 351, by drying mixed with sand

in the air oven at about $110^{\circ}\text{C}.$, but in presence of unsaturated fatty acids considerable oxidation may occur, and it is probably as accurate and much quicker, to heat 2-3 grm. in an uncovered and somewhat inclined platinum crucible over a small flame, till a slight crackling, accompanied by tiny puffs of smoke, indicates that the whole of the water is expelled. According to Fahrion,* the difference between the two methods does not on the average exceed 0.2 per cent. If the crucible be rapidly cooled on an iron block, the entire operation need not take more than 15 minutes. In cases where much solid matter is present or from any cause such as the presence of soaps, the *dégras* does not readily liquefy, it is preferable to add it to a known weight of oil or fat from which the moisture has been already expelled. In place of heating till smoke is produced, the melted fat may be stirred with a small (high temperature) thermometer weighed in with it, retaining the temperature within say $150^{\circ}\text{C}.$

A useful comparative idea of the water present in *dégras* and other fat emulsions may be obtained by shaking 50 c.c. of the material in a 100 c.c. cylinder with 25 or 50 c.c. of ordinary petroleum lamp oil, and allowing the mixture to stand in a warm place until it has separated into two layers; deducting the volume of petroleum oil added; the upper layer represents the oil soluble in petroleum, while the lower consists of water, lime- and alkali-soaps, and oxidised fatty acids insoluble in petroleum.

Several methods have been proposed for the determination of the specific gravity of *dégras*, of which the best seems to be that of Galowski, † who employs an Erlenmeyer flask of which the neck is ground to fit a flat glass plate, though with care an ordinary conical flask may be used, filled accurately level with the top. The flask is weighed empty ($= T$), and filled with water ($= W + T$), carefully dried and again filled two-thirds full with the well mixed *dégras*, and again weighed ($= T + D$). It is now kept for an hour or two at a temperature of 60° - $80^{\circ}\text{C}.$; water is added to about three-quarters of the total volume of the flask, and heated to gentle boiling till all air is expelled, which is often present in considerable quantity in the form of small bubbles. The flask is then cooled, filled with water to the

* *Zeits. f. angew. Chem.*, 1891, p. 172.

† *Gerber Zeitung*, 1902, No. 53; 1903, No. 1; *Collegium*, 1903, p. 5.

brim, and weighed ($= W_1 + T + D$). The calculation, precisely similar to that on p. 7, is as follows:—

$$\text{sp. gr.} = \frac{(T + D) - T}{(W + T) - T - (W_1 + T + D) + (T + D)}$$

Thus, if $T = 28$ grm., $T + D = 108$ grm., $T + W = 130$ grm., and $W_1 + T + D = 128$ grm., we have

$$\frac{108 - 28}{130 - 28 - 128 + 108} = \frac{80}{82} = 0.976$$

as the specific gravity of the original dégras. The gravity of the oils may also be determined in an ordinary pycnometer by allowing the dégras to stand in a cylinder in a warm place till a sufficient quantity has separated, and if the water, ash, and gravity and quantity of the unsaponifiables be also determined, the experienced chemist has the most important points for judging of commercial value. Obviously the weight of water and ash deducted from 100 will give the weight of oils, and the weight of unsaponifiables further deducted that of saponifiable oils, while from these figures and the specific gravities of unsaponifiables and total oil the gravity of the saponifiable oils may be inferred. As the gravity of the principal oils used in chamoising does not exceed about 0.928, a higher value roughly indicates the degree of oxidation and the proportion of oxidised acids likely to be present. From the gravity of the unseparated dégras and that of the oils, the percentage of water may be approximately calculated, if the ash is negligible.

Ash should be determined by heating 10–20 grm. of the material in an inclined crucible, the side of which only is in contact with the flame. If the operation is properly conducted, the water first escapes without spurting, and the fat then takes fire and burns quietly. The ash in a genuine dégras pressed out of chamoised skins should not reach 0.1 per cent., and in one separated by lye and acid it may reach 0.3 per cent., but should not be much over 0.5 per cent. Except as an indication of the mode of production, or of intentional adulteration, the only constituent of the ash which need be separately determined

is iron, since if present in considerable quantity, it darkens the colour of the leather.

The dégras or sod-oil should be tested with litmus paper, and if found to be acid, a portion should be washed with water, which should be titrated for mineral acids with methyl orange or lacmoid as indicators. Addition of petroleum ether before washing will often facilitate the operation. If much matter insoluble in petroleum spirit is present in the dégras (which must be first freed from water as above described), it should be determined by the methods given on p. 314. Soap, produced by the action of the alkaline lye, is often found in dégras separated by its means, and in sod-oil. This tends to make the dégras sticky and viscous, and to hinder its penetration in the leather. Where soap is present, the ash will of course be alkaline.

The oxidised fatty acids may be determined as on p. 314. In genuine pure dégras reckoned to 20 per cent. of water, these oxidised fatty acids should reach 12 per cent., but in judging from this of the quality, it must be remembered that if the oxidation has gone so far as to leave the dégras sticky and incapable of penetrating the leather, its other constituents will be of much less value. The percentage of oxidised acids simply depends on the oxidisability of the oil, and the stage to which oxidation has been carried. Jean* proposed to make a distinction between the oxidised fatty acids of which the soap could be salted out, and those which were soluble in brine; but Fahrion† has shown that portions, both of oxidised and unoxidised fatty acids, are soluble in both water and petroleum ether, and that some of their soaps are soluble in salt solution, while others are precipitated, together with peptones from the skin which are often present. The soluble fatty acids amounting to about 5 per cent. are in any case removed by the washing water, and the results, both in oxidised and unoxidised acids, apply only to the insoluble acids (Hehner value).

Unsaponifiable matter over 2 or 3 per cent. either indicates adulteration with mineral or rosin oil, or the presence of wool-fat or possibly the use of shark-liver oil or some other oil containing liquid waxes in the chamoising, for which, however, such oils are very unsuitable (p. 335). . . . Adulteration with hydrocarbon oils

* *Mém. Scientif.*, 15, 889; *Wess.-Tech. Beilage des Ledermarkt*, 1900, p. 37.

† *Zeit. angew. Ch.*, 1902, Heft 49; *Collegium*, 1903, p. 2.

is not likely to be to a less extent than 10 or 15 per cent., or it will hardly pay. The natural unsaponifiable matter of *dégras*, consisting principally of cholesterols and higher alcohols, is always solid, while hydrocarbon oils are liquid. The detection of wool-fat is less easy, since cholesterols are always present in the oils used for chamoising. It is probable that the different proportions of the fat saponified in the usual way and under pressure, or by the aid of metallic sodium, might afford useful indications (p. 310). The presence of a middle layer between the petroleum ether and the soap solution in shaking out unsaponifiables is always suspicious, either of wool-fat or other liquid waxes. It consists either of high alcohols insoluble in petroleum ether, or of soaps of high fatty acids insoluble in water, or both.* If it refuses to disappear on the addition of alcohol to the solutions and sufficient standing, it must be retained with the soap solution and wash waters, and subsequently filtered off on a tared filter, dried at 100° C. and estimated separately.

In place of shaking out the unsaponifiables from the soap solution, Baldracco† recommends extraction of the dry soap with petroleum ether as giving more concordant results. His method, which is adopted by the Italian customs, is as follows:—

15–20 grm. of the *dégras* is accurately weighed into a small flask, and saponified on the water-bath for 2–2½ hours with 5 grm. potassium hydrate, 50 c.c. of strong alcohol and a little water, using a reflux condenser. The greater part of the alcohol is now distilled off, and the liquid transferred to a small basin which is retained on the water-bath till the last traces of alcohol are expelled, when 8 grm. of hydric sodic carbonate to carbonate the excess of caustic, and 50–60 grm. of washed and ignited quartz sand are added, and well mixed with a glass rod, and the mass is dried in an oven at 110° C. till it becomes solid. It is now well pulverised and placed in a paper “thimble” in a Soxhlet apparatus and extracted thoroughly with petroleum ether boiling below 75°. The ethereal solution is washed repeatedly with water till perfectly neutral, and finally the ether is distilled off, and the residue dried to constant weight, first on a water-bath and finally in a drying oven at 110°. This

* Cp. Lewkowitsch, *Journ. Soc. Chem. Ind.*, 1892, p. 136.

† *Collegium*, 1904, p. 333.

method, of course, avoids any difficulty with the middle layer above mentioned.

Acid-, saponification-, and iodine-values are best determined, or at least reckoned, on the fatty matters soluble in petroleum ether, and hence free from water, non-fats, and the oxidised fatty acids which are insoluble in this medium, as otherwise they are so varied by the presence of these bodies as to be useless for comparison. The acid value is of course high in *dégras* which has been treated with alkaline lyes and subsequently with acids. The saponification value of a genuine *dégras* cannot well be lower than that of the oil from which it is made, and will generally be considerably higher from the formation of acids of low molecular weight by the oxidation. In the purified fat from an old and much oxidised German *dégras* analysed by Schmitz-Dumont, it even reached 234, and is frequently as high as 200. If it falls below 180, adulteration with unsaponifiable oils may be assumed. The iodine value is always lower, and generally much lower than that of the original oils. It is, of course, lowered still further by the addition of mineral oils, but may be as low as 50-60 in a genuine *moëllon*. Hence its determination is usually unimportant,* except as a measure of oxidation.

As unsaponifiable hydrocarbons from petroleum and other sources are now frequently used intentionally for leather manufacture, and still more often as adulterants, they must here be briefly described.

Rosin or Resin Oils are obtained by the destructive distillation of ordinary rosin, and subsequent fractionation of the product. The specific gravity of the heavier portion, which alone is used for adulterating fish oils, is 0.96-0.99, and is therefore lighter than water, but heavier than mineral oils or than any of the true saponifiable oils, and its principal object is to correct the lower gravity of mineral oils. Rosin oils are fluorescent and usually contain unaltered resin acids, but consist principally of aromatic hydrocarbons allied to the terpenes. They have decided antiseptic properties, and in moderate quantities are probably useful in checking the growth of mould on leather. Crude rosin oils, from the resin acids they contain, may have a decided saponification value, and both the resin acids

and the aromatic hydrocarbons absorb iodine. A rosin oil examined by Schmitz-Dumont had an iodine value of 69.3. For the determination of rosin, see p. 316.

Mineral Oils.—These are either distillation-products of petroleum, or derived from the distillation of petroleum-yielding shales. They consist mainly of hydrocarbons of the paraffin, olefine and naphthene series, of very variable molecular weight, boiling point, and specific gravity. The higher members of the paraffin series are crystalline solids (paraffin wax) with melting points varying from 45° to 70° C., the lower are volatile liquids boiling at low temperatures, such as are contained in petroleum ether (light petroleum spirit) boiling at from 50° to 70° C. Immediately there are oils of higher boiling point, mostly used as burning oils. The viscous non-crystalline products known as vaseline and vaseline oils, are mixtures of paraffins with naphthenes, and olefines of high boiling point. The naphthene series are isomeric with the olefines, but are saturated ring compounds (cyclic hydrocarbons), allied to the aromatic series. A good deal of information on the chemistry of petroleum is given in Allen's 'Commercial Organic Analysis,' vol. ii. From the percentage of olefines, and perhaps other unsaturated carbon compounds contained in petroleum, the liquid portions have a distinct iodine value. Thus a number of "vaseline" oils examined by Schmitz-Dumont gave iodine values varying from 9 to 19. From similar reasons they have a low but appreciable temperature reaction with sulphuric acid (p. 299). The iodine value of solid paraffins is much lower than that of the oils. Petroleum oils have practically no saponification value. The specific gravity even of the heavier petroleum oils is generally lower than that of glyceride oils, the heaviest American cylinder oils only reaching 0.9, and vaseline and Russian cylinder oil about 0.925. At the same time, their refractive index is considerably greater, and their refractive constant, calculated by Gladstone and Dale's method by dividing the refractive index minus one by the specific gravity, is about 0.545 or over, while most fatty oils vary from 0.510 to 0.525. If the refractive constant of a pure oil is known, its determination in an unknown sample is a rapid method of detecting, and even of estimating, adulteration with mineral oil. The refractive constant of rosin oil is also very high. For distinction of mineral and rosin oils from each other and from the

cholesterol and other unsaponifiable bodies naturally present in oils, see p. 313.

Mineral Waxes.—Though the term "wax" is commonly applied to these products from appearance and general properties, their chemical constitution is very different to that of the true waxes (p. 281), as they consist entirely of unsaponifiable hydrocarbons, while true waxes are compounds of fatty acids with the higher monatomic alcohols.

Paraffin Wax consists principally of the higher members of the paraffin series of saturated hydrocarbons of the general formula $C_n H_{2n+2}$. It exists in varying properties in most petroleum, from which it crystallises on cooling, but its present principal source is the Scottish oil distilled from shale, which it sometimes forms so large a proportion as 15 per cent. The crude paraffin wax, which separates on cooling from the heavy part of the distillate, is known as "scale," and is purified by pressing, bleaching, etc. The melting point varies with the mixture of hydrocarbons present, and consequently with the source. That melting below 48°C. (118°Fahr.) is known as "soft" wax; that over 48.9°C. (120°Fahr.) is "hard." Melting points up to 60°C. (140°Fahr.) are, however, attained in some samples. The determination in England is made by a method practically identical with Shukoff's, and the latter is likely to be adopted by the German manufacturers of paraffin from distilled lignite. No actual rise of temperature is usually noted with paraffin, but the temperature remains constant for perhaps half a minute. The present German official method is to melt a small piece of the wax on water of 70°C. contained in a small beaker (7 cm. high, 4 cm. diam.), so as to form a disc of about 6 mm. diameter. The beaker is allowed to cool slowly and the point noted at which a film appears on the surface of the paraffin. In the American method about 50 grm. is melted in a hemispherical dish of about $3\frac{1}{2}$ in. diam. and the point at which "filming" occurs is noted with a round bulb thermometer, of which the bulb is only three-quarters immersed. Both these methods are much less accurate than Shukoff's. The capillary tube method is sometimes used and gives concordant results, which in pure paraffin waxes differ little from Shukoff's.

Specific gravity of paraffin waxes varies from 0.87 to 0.91 at 15°C. ; and for the liquid wax at the boiling point of water,

from 0.748 to 0.757; the gravity being highest for the hardest waxes.

Paraffin waxes are scarcely soluble in absolute alcohol, but easily so in the common oil solvents, though only to a limited extent, strong hot solutions crystallising on cooling.

Ceresin is a mineral waxy substance obtained from ozokerite, a mineral occurring in Galicia, and in many other petroleum-yielding districts. In many respects it closely resembles paraffin wax, but has a much higher melting point varying from 61° C. (141.8° Fahr.) to 78° C. (172.4° Fahr.), and certain varieties even reaching 80° C. Consisting as it does of a natural mixture of various constituents, its apparent melting point varies with the method used. Ceresin is principally used to harden the paraffin waxes used for candles, and is generally too dear for use as a stuffing grease, for which its high melting point also renders it less generally suitable than paraffin. It is frequently adulterated with bleached rosin and paraffin wax. Its texture is harder and less crystalline than paraffin wax, and it is less soluble in many solvents. Paraffin wax may be detected in ceresin by heating in absolute alcohol in which the latter is almost absolutely insoluble, while if paraffin is present, the liquid will leave a crystalline residue if evaporated on a microscope slip.

Animal and Vegetable Waxes.—These are mostly true waxes, consisting of higher fatty acids combined with the higher monatomic alcohols instead of with glycerine as in the true fats. Japan wax is, however, chemically a glyceride.

Beeswax.—Most unbleached beeswax is yellow, but may vary to green or brown in some genuine foreign waxes. White wax is produced by bleaching in sunlight, or by oxidising agents, and is of greater specific gravity and more brittle than the original wax. To facilitate the process and lessen the brittleness, 3-5 per cent. of tallow and a little turpentine are frequently added before bleaching. Genuine wax always contains pollen grains, which may be detected under the microscope. Beeswax is soluble in the usual fat solvents, carbon disulphide, petroleum ether, chloroform, etc., and in ether by the aid of heat. It is quite insoluble in cold alcohol, but about 90 per cent. of the total is soluble in boiling alcohol, of which the principal part separates on cooling.

Beeswax is frequently adulterated with ceresin or paraffin wax, rosin, and stearic acid. Its complete analysis is too com-

plicated to be given here, and other books, such as Lewkowitsch's 'Oils, Fats, and Waxes' must be consulted, but a few particulars may be given. Beeswax consists mainly of free cerotic acid (probably $C_{27}H_{54}O_2$), an acid of the stearic series, and of myricyl palmitate (myricin), together with small quantities of other alcohols, acids, and hydrocarbons. Myricyl alcohol is probably $C_{31}H_{64}O$. The acid and saponification value can be found by the usual methods (p. 304), but as some waxes are not easily saponified, it is probably better to completely saponify by pouring 20 grm. of the melted wax into a boiling solution of 20 grm. of potassium hydrate in 15 c.c. of water, and after heating and stirring vigorously for 10 minutes to decompose the soap with excess of hydrochloric acid, and wash, and separate the free acids and alcohols, and determine the total acid value in the dried "decomposed wax" dissolved in hot neutral alcohol. Lewkowitsch points out that as the myricin assimilates the elements of water, during decomposition, it is necessary to divide the difference between the acid value of the original wax and that of the "decomposed wax" by 0.974 to obtain the "ether value" of the original wax. The total acid value of the decomposed wax may vary in genuine samples from 88-93 and the acid value from 18-20 in yellow wax to 22 in bleached waxes. Mixtures of Japan wax, stearin and ceresin are however easily made which will give corresponding values.

The gravity of beeswax at $15^{\circ}C$. is about 0.96 to 0.97. Addition of ceresin and paraffin wax lowers this, and of course lowers the acid- and saponification-values; but there is no satisfactory method for the direct detection of small quantities of these adulterants. The detection of carnauba wax is still more difficult. Resin or resin acids may be detected by the Liebermann-Storch reaction with acetic anhydride and sulphuric acid (p. 316). For resins, Twitchell's process may also be applied quantitatively after first removing unsaponifiables by shaking out. Stearic acid may, in absence of resin acids, be detected by boiling 1 grm. of wax with 10 c.c. of 80 per cent. alcohol, filtering the cooled solution and adding water by which stearic acid is separated. Pure beeswax may give slight opalescence.

Carnauba wax is now largely used as a constituent of shoe-pastes and the like, as it is considerably cheaper than beeswax. It is exuded by the leaves of a South American palm,

Corypha cerifera, and in its crude form is greenish or yellowish, and so brittle and hard that it can be easily powdered. It can be bleached almost white. It is almost completely soluble in ether and boiling alcohol, and the alcoholic solution deposits a crystalline mass on cooling with a melting point of 105°C . The melting and solidifying points of the original wax lie between 80° and 90°C . It contains a little free acid, apparently cerotic, and consists mainly of the ester of an acid, probably cerotic, but possibly of somewhat lower molecular weight (carnaubic). It is saponified by alcoholic potash with great difficulty. It contains about 55 per cent. of unsaponifiables (alcohols and hydrocarbons), and its saponification value is about 80. For constants, see p. 350.

Japan wax is not chemically a true wax, but a hard fat, consisting principally of palmitin and palmitic acid, with a small quantity of a dibasic acid (Japanic) $\text{C}_{20}\text{H}_{40}(\text{COOH})_2$, which in Lewkowitsch's opinion probably forms a mixed glyceride with palmitic acid. Japan wax is insoluble in cold alcohol, but readily soluble at a boiling temperature, separating again almost entirely on cooling. It is soluble in most of the ordinary oil solvents. It contains $1-1\frac{1}{2}$ per cent. of unsaponifiables, and has a saponification value of about 220, and a very low iodine value. Its solidifying point is about 50°C . Its sp. gr. is equal to water at about $16^{\circ}-20^{\circ}\text{C}$.

Japan wax is a hard somewhat crystalline mass of a pale greenish yellow tint which darkens with age. It is obtained from the berries of several sumachs (*Rhus*). It is frequently adulterated with perilla oil, of which even small quantities materially raise the iodine value. It is also adulterated with water and with starch.

I.—TABLE OF CONSTANTS OF LIQUID OILS.

Name of Oil.	Sp. Gr. 15° C.	Refract. Index 15° C.	Solidifying Temp.	Refract. Constant ($\frac{n-1}{d}$)	Saponi- fication Value.	Iodine Value.	Sp. Temp Reac
Blown seal	'981	under '5	221	78	..
„ cottonseed	'974	under '5	213	56	227
„ rape	'967	1'481	..	'497	200	63	253
Castor	'965	1'480	- 18°	'495	180	84	90
Raw linseed	'935	1'484	- 16° to - 20°	'518	193	175	336
Cod liver (medicinal) ..	'926	1'485	0° to - 10°	'524	185	146	272
„ Moller's	'928	1'481	..	'518	..	165	..
„ (brown)	'928	1'482	..	'523	185	..	245
Coast cod (mixed livers) ..	'930	1'482	..	'518	185	172	..
Whale	'931	1'476	- 2° (partial)	'517	193	118	157
Sardine (Japanese)	'916	1'479	20°	'523	192	121	..
Seal (pale)	'925	1'478	- 2° to - 3°	'517	189	138	220
Shark liver (<i>Scymnus</i>) ..	'916	1'478	- 16°	'522	168	102	..
Mixed fish	'929	1'480	..	'516	184	140	184
Cottonseed	'925	1'475	- 12°	'514	193	108	167
Arachis ("earth nut") ..	'922	1'474	- 1°	'512	193	94	132
Maize	'922	1'477	- 10°	'517	190	118	..
Sesame	'921	1'475	- 5°	'512	190	108	150
Olive	'916	1'471	- 2° to + 4°	'515	193	83	92
Rape (colza)	'915	1'474	- 2° to - 10°	'518	176	101	125-1.
Neatsfoot	'915	1'474	"Tender"	'518	193	70	93
Lard (oil)	'912	1'472	- 8° to + 6°	'517	193	79	90
Tallow (oil)	'903	1'469	"Tender"	'519	90
Sheepskin grease (oil)	1'468	"Tender"	'510	197	60	90
Egg yolk, hen (oil)	1'466	Liquefies	..	190	50-70	..
„ duck	1'466	20°-23°	35-40	..
Sperm	'884	1'468	Deposits spermaceti	'528	135	84	100
Distilled wool oleine ..	About '900	High	120-150
Mineral oil (for leather) ..	'85-'92	1'47- 1'51	..	'545-'555	Nil	Up to 26	Very low
Rosin oil	'96-'99	1'50- 1'54	..	'525-'545	Resin acids	43-48	..

The solidifying temperatures and iodine values of oils vary much with the amounts of saturated fats they contain.

II.—TABLE OF CONSTANTS OF FATS.

Name of Fat.	Sp. Gr. 98°-100°.	Sp. Gr. 60° C.	Refract. Index 60° C.	Refract. Const. ($n - 1$) d	Melting Temp.	Solidi- fying Temp.	Saponi- fication Value.	Iodine Value.
					degrees	degrees		
Purified wool-fat	'902	'885	1'465	'525	102	27
Japan wax	'876	'907	1'450	'495	52-56	45-50	221	5'8
"Oleo-stearine"	'875	'907	1'449	'495	54	..	203	31
Coconut oil	'874	'897	1'442	'493	23-28	14-20	255	8'7
Palmnut oil	'873	'896	1'443	'495	23-28	20	247	13'5
Butter fat	'868	'895	1'450	'503	31-35	19-25	227	30
Mutton tallow	'859	'895	1'442	'494	47-50	44-45	195	40
Beef tallow	'861	'901	1'442	'490	43-45	36-38	196	42
Horse fat	'861	'894	1'455	'509	34-39	20-30	197	79
Bone fat	'894	1'451	'504	21-22	15-17	191	51
Lard	'861	'886	1'452	'510	36-44	32-39	196	59
Palm oil	'859	'883	1'452	'512	30-34	21-25	202	52
Cacao butter	'858	'887	1'450	'507	25-33	22-27	197	35
Carnaüba wax	'842	85	78	87	13'5
Distilled grease stearine	'836	..	1'445	'514	48-57	45-53	Up to 195	..
Beeswax	'822	62-63	62-63	102	9'6
Vaseline	'832	'851	1'470	'553	Nil	14-26
Paraffin wax	'752	'776	1'434	'559	40-55	40-55	Nil	4

III.—TABLE OF CONSTANTS OF FATTY ACIDS.

Name of Fatty Acid.	Sp. Gr. 98°-100°.	Sp. Gr. 60° C. or 70° C.	Refract. Index 60° C.	Refract. Const. ($n - 1$) d	Melting Temp.	Solidify- ing Temp.	Saponi- fication Value.	Iodine Value.
					degrees	degrees		
Stearic acid	'850	'865	1'433	'500	71	..	197'5	Trace
Palmitic acid	'835	'862	1'432	'501	62	..	219'1	Trace
Oleic acid	'847	'870	1'447	'514	14	4	198'8	90
Mixed tallow acids ..	'845	'875	1'442	'505	44	44-54	197	About 40
Mixed olive oil acids ..	'843	'873	1'446	'508	26	17-23
Mixed cod oil acids ..	'858	'882	1'458	'519	..	18	204	..
" " Moller's	'876	'900	1'464	'515

The numbers given in the foregoing tables must be taken as approximate only, and representing the average character of a pure oil. Considerable divergence occurs between perfectly genuine samples of the same oil, and several of the constants are influenced by age and oxidation.



SECTION XXI.

ANALYSIS OF COMMERCIAL PRESERVED EGG-YOLK.

EGG-YOLK is somewhat largely used in leather manufacture as a softening and filling material for the finer leathers, acting as a sort of natural fat liquor on account of the large amount (about 30 per cent.) of oil which it contains. Probably the earliest method for its technical analysis is due to Kathreiner, and in principle this is still in use, but as material improvements in detail have been made, the latest form as recommended for adoption by the International Association of Leather Trades Chemists by a Commission appointed at their Conference of 1904 will be described.

"*Sampling*.—Samples should only be taken after the cask of yolk has been rolled for a quarter of an hour, and well stirred with a stick. Each sample should be of about 200 grm. and should be preserved in a wide-mouthed bottle which should be filled, well corked, and sealed. If an average sample from a number of casks is to be taken, the individual portions are well mixed with a spatula in a vessel of sufficient size before placing in bottles.

"*Rapid Commercial Analysis* includes—

1. Determination of moisture,
2. " " fatty matters,
3. " " common salt,
4. " " total ash.

"1. *Determination of Water*.—The sample is well mixed, and 15–20 grm. are weighed into a flat-bottomed basin, which has been previously tared, including a short glass rod, and a little dry sand.* The sand and yolk are well mixed, and placed in.

* Kathreiner's original directions are as follows: About 30 grm. of sand, previously treated with HCl and well washed, and ignited, are placed in a flat basin of 2½–3 inches diam. and ½–¾ inch deep. A glass rod about 3 inches long is added, and the whole after drying at 110° C., is cooled and weighed. 3–5 grm. yolk are now added, and quickly weighed before mixing. The basin is then placed on black glazed paper, and sand and egg carefully mixed with the rod and dried in the air-oven for two hours at 105°–110° C., and again placed on glazed paper and the hardened surface cut through and broken up with a scalpel. It is returned to the oven and dried till it ceases to lose weight.

the drying oven, and at first dried slowly, care being taken to break up the mass as it solidifies. The drying is continued at 100° – 105° C. to constant weight, and the loss is calculated per 100 grm. of yolk. If boric acid is absent, the quantity taken may be conveniently reduced to 10 grm.

"2. *Determination of Fatty Matters.*—The dry residue is detached from the basin as completely as possible and is transferred to a 'thimble' of paper,* and placed in a Soxhlet extractor, and exhausted with petroleum ether boiling at 70° – 75° C. till the liquid which syphons is perfectly colourless. For very exact extraction the contents of the thimble are now emptied into a small mortar, rapidly dried, and powdered, and returned to the thimble, and again extracted with the same liquid as before, till the apparatus has syphoned four or five times.

"The greater part of the petroleum ether is distilled off, and the remainder of the fat solution is transferred to a tared beaker and dried in the oven at 100° – 105° C. till the petroleum ether is completely eliminated, which should require at most an hour. The weight of residue is calculated to 100 grm. of yolk, and the solvent employed is mentioned in the analytical report.

"Where boric acid is present, a certain proportion is extracted with the solvent along with the fats, and it is necessary to determine this, and deduct it from the fats found. To detect boric acid qualitatively in the fatty matters, 0.5 grm. of the latter is shaken with a few c.c. of warm methyl-alcohol (not "methylated spirit") which is decanted and inflamed, when, if boric acid is present, it will burn with a green flame. If this prove to be the case, 2 grm. of the fatty matter are dissolved in a little petroleum ether, and are shaken two or three times with distilled water at 36° C. in a separating funnel, the aqueous solutions are united, 20 c.c. of neutral glycerine is added, and a little phenolphthalein, and the solution is titrated with N/1 NaOH to distinct redness. Each c.c. corresponds to 0.0613 grm. of boric acid, BO_3H_3 , and the amount must be calculated to the totality of fatty matter found, and deducted from its weight.†

* Schleicher and Schull.

† It is obvious that in place of determining the boric acid and deducting, it may be removed by washing the whole of the petroleum ether extract with water before distilling off the ether, but if this is done the precautions must be adopted to get rid of water in the ether which are described in connection with the determination of unsaponifiables on p. 310, or much trouble will be involved in drying to constant weight.

3. *Determination of Common Salt*.—The paper thimble is removed from the Soxhlet, dried in the oven to remove petroleum ether, and placed in a funnel, in the neck of a 250 c.c. flask, and washed with hot water till the volume is made up to 250 c.c. The salt is determined volumetrically in a measured portion of the solution with $N/10$ silver nitrate and potassium chromate (p. 39).

“4. *Determination of Ash*.—10 grm. of the yolk are weighed into a platinum basin, dried, and carbonised at a low temperature. The carbon is treated in the basin with boiling water, taking care not to break the carbonaceous mass, the liquid is decanted, the carbon dried and ignited to white ash, the wash waters are added to the basin and evaporated to dryness, heated to 110° – 120° C., and weighed.

“If the difference between the ash and the common salt found by titration, exceeds $1\frac{1}{2}$ per cent., the ash must be examined for borax and other mineral additions.”

It is by no means indifferent what solvent is used for the fat-extraction. Jean * gives the results of fat-extraction with various solvents on dry egg-yolk as follows:—

Petroleum ether	48.24 per cent. oil.
Ethyl ether	50.83 " "
Carbon disulphide	50.45 " "
Carbon tetrachloride	50.30 " "
Chloroform	57.66 " "

Jean points out that the large excess extracted by chloroform consists of lecithin and cholesterol, but mentions that even chloroform does not extract the whole of the lecithin. Ethyl ether dissolves a small part of the lecithin, and also a portion of the sodium chloride, whilst petroleum ether dissolves the fats only. The lecithin contained in yolk is a complex body, containing stearic and palmitic acids in combination with cholin and glycerophosphoric acid, and it may consequently be estimated in the absence of other phosphorus compounds by a determination of that element, of which the stearo-palmitic lecithin contains 3.98 per cent., which is equivalent to 12.58 per cent. of PO_4H_3 . Vignon and Meunier † therefore propose extraction with chloroform, which they state removes the whole of the lecithin, and

Collegium, 1903, p. 71.

† Op. cit., 1904, pp. 325 et seq.

subsequent determination of phosphorus in a portion of the extracted fat, of which they advise 2 grm. to be gently ignited in a platinum basin over a Bunsen burner with 6 grm. of a mixture containing 25 per cent. of dry sodium carbonate, 25 per cent. of dry potassium carbonate, and 50 per cent. of potassium nitrate. The fused mass is dissolved in dilute hydrochloric acid neutralised with soda, and slightly acidified with acetic acid, and titrated with standard uranium acetate solution in the usual way. They found an average of 2.33 per cent. of phosphoric acid in the yolks of hens' eggs, and 1.91 per cent. in ducks', corresponding respectively to 18.5 per cent. and 15.2 per cent. of lecithin, and these numbers were very constant.

Egg-oil is mainly a glyceride of oleic acid, but containing a considerable quantity of palmitic and possibly of stearic acid. Its refractive index is about 1.466 at 20° C., its saponification value 188, and it contains about 2.7 per cent. of crystalline unsaponifiable matter, probably cholesterol. Its iodine value, according to the authors just quoted, is on the average 52 for hens', and 37 for ducks' eggs. None of these numbers are very characteristic, lying between those of the non-drying oils and the soft fats. The determination of phosphorus in the extracted fats probably gives the best guarantee of their freedom from foreign admixture.

The water contained in natural egg-yolk was found by the authors cited to be somewhat variable, averaging 51 per cent. for hens' eggs (max. 55.9 per cent., min. 42.7 per cent.). For ducks' eggs, the average was 44.9 (max. 47.3 per cent., min. 40.9 per cent.).

The fatty matters are, of course, the most important constituent of egg-yolk commercially. For pure egg-yolk, with chloroform extraction, the authors cited give 32.5 per cent. (max. 33.5 per cent., min. 30.7 per cent.) for hens' eggs, and 39.0 per cent. (max. 39.7 per cent., min. 37.9 per cent.) of fats, including lecithin. With petroleum ether the average for hens' eggs was 29.5 per cent. (max. 32.7 per cent., min. 26.4 per cent.), Jean gives 28 per cent. Vignon and Meunier give no corresponding figure for ducks' eggs, but presumably it would be about 33 per cent. It is obvious that accepting a definite standard of oil in natural yolk, it would be easy to calculate the natural yolk present in any commercial preserved yolk, but as natural yolk is

somewhat variable, and the oil constitutes the main value, there is no object in doing this, and it is better to value on the oil direct, so long as there is no suspicion of the admixture of foreign oils. No very precise statistics are available as to the amount of fats in commercial preserved yolk, but in "Chinese yolk" from ducks' eggs, it seems to average about 21 to 23 per cent., and this is also about the amount contained in European preserved yolk.

The following references include the literature which has been referred to by the author, and, it is believed, all of importance which has appeared in recent years.

- F. Jean, Congrès du Ch. appliq., 1900, p. 482.
 „ Collegium, 1903, p. 71.
 E. Carpiaux, "L'œuf de poule," Bruxelles, 1903.
 M. S. Bruère, Collegium, 1903, p. 45.
 Kathreiner and Schorlemmer, Collegium, 1903, pp. 134, 137.
 Vignon and Meunier, Collegium, 1904, pp. 325, 335.
 Schorlemmer and Sichling, Collegium, 1906, p. 90.
 I.A.L.T.C. Commission, Collegium, 1906, p. 242.

SECTION XXII.

THE ANALYSIS OF LEATHER.

THE analysis of leather may have for its object either the detection of weighting substances, or of insufficient tanning, or the discovery of the method and materials used in its manufacture, or of errors in its production; and it is obvious that the scheme of analysis adopted must vary very widely, not only with the object in view, but on account of the very diverse sorts of leather which the chemist is called upon to examine. Some effort has been made in the following pages to meet these varying requirements, but it is obvious that it is impossible to provide for all cases which may occur in practice, and much must be left to the ingenuity of the individual chemist.

Preparation for Analysis.—It is of the first importance that the portion of the sample used for extraction should be reduced to a fine state of division, and where the leather is tolerably hard

and free from grease, as in the case of sole leather, or even the more lightly stuffed kinds of curried goods, it may, after cutting in small pieces, be advantageously ground in a mill similar to that employed for tanning materials. Where this is not practicable, recourse must be had to shaving or shredding with a knife or sharp chisel, or with a "whitening sleeker."^f

Dr. A. Turnbull has constructed a machine consisting of a shoe-manufacturers' heel-paring cutter, mounted on a small lathe-head, which reduces the leather effectively, but is not on the market commercially. If the sample of leather is of sufficient size the ordinary shaving or whitening machine will render good service, but it is inapplicable to small pieces, and it is difficult to secure an even proportion of grain and inner fibre, which may differ widely in their proportion of fats, etc.

In japanned and enamelled leathers it is often well to remove the layer of japan mechanically, and subject it to analysis separate from the body of the leather. In dyed leathers, the dye must generally be examined by the direct application of reagents to the surface, for which no general scheme can be given, though some information can be obtained from the tables devised from textiles.* Many dyes may be extracted with alcohol, and examined by the methods given in Section XXIII. The ash analysis of dyed leathers is often complicated by the presence of iron, chromium, and other bases used as mordants, and it is difficult to judge whether these have been simply used for this purpose, or have formed part of the material of a mixed tannage.

The general scheme of a commercial analysis is usually as follows :—

Moisture.

Fatty matters (extracted by carbon disulphide or petroleum ether).

Water-soluble matters	.	{	Uncombined tannins.
		{	Non-tannins (glucose, dextrine, etc.).
Insoluble leather fibre	.	{	Hide substance, by Kjeldahl.
		{	Fixed tanning matters.

(The above should add up to 100 per cent.)

Mineral Ash.—(This must not be added in with the above, unless it is separately determined in the soluble and insoluble portions and deducted.) The mineral ash can of course be

* See Tables of Lehne and Rusterholz published in the Journ. Soc. Chem. Ind., 1895; and the later ones for animal fibres of Green, Journ. Soc. Dyers and Colourists, 1905, xxi. p. 236, abstracted in Journ. Soc. Chem. Ind., 1905, pp. 1034 *et seq.*

further analysed in the case of chrome and other mineral and combination leathers or to detect mineral adulterations. In most vegetable leathers it will not exceed 1 per cent. and will consist mainly of lime.

Determination of Moisture.—As most oils oxidise readily, especially when finely divided, as on the leather fibre, and give rise partly to volatile compounds, and partly to fixed resinous bodies often heavier than the original oils, no great accuracy can be expected from the ordinary method of drying at $100^{\circ}\text{C}.$, and approximate constancy only should be aimed at; and to shorten the drying, moisture should be determined on a small separate portion. In many instances it will be sufficient, and perhaps even more accurate, to calculate moisture from the loss after determining fats and insoluble matter, rather than by direct drying. If an extremely accurate determination must be made, the drying should take place *in vacuo* or an atmosphere of CO_2 or coal-gas. Probably the greatest accuracy would be reached by drying in a tube heated to $100^{\circ}\text{C}.$ in a current of inert and dry gas, and collecting the moisture in a calcium-chloride tube as in organic analysis. As leather-fibre obstinately retains a portion of moisture, the results are sure to vary with the method adopted; and samples are rarely received in a condition in which an accurate moisture determination is possible. Some chemists calculate to a fixed amount, 14 or 15 per cent., but it must be remembered that in the presence of glucose or a deliquescent salt the moisture will usually exceed that of a normal leather.

Determination of Fats.—25 grm. of the finely divided sample is weighed, and placed in a large Soxhlet apparatus. It will generally be best to put a little cotton-wool (free from fats) in the bottom of the extraction chamber, then the leather, and afterwards a pad of cotton-wool to distribute the solvent and prevent loss, but, if preferred, an inner-tube or a filter-paper may be used (p. 352). The extraction must be somewhat long, especially if the leather is not finely divided, and it is safest to use two flasks. Carbon disulphide or petroleum ether is preferable to ordinary ether. The solvent is distilled off and the oil estimated as on p. 287. After draining the solvent as completely as possible from the leather residue, the contents of the Soxhlet are turned out into a weighed basin, and dried first on the water-bath, and afterwards in the air or water-oven till constant, the

cotton-wool being easily removed from the dry leather, and preserved for future use. If oxidisable oils have been used on the leather, they will not be wholly removed by this process, as some at least of their products are insoluble in petroleum ether, and similar solvents. A further portion may be removed by extraction with absolute alcohol, but if resinous matters or "reds" from the tanning matters are present, they will also be dissolved; and generally such oils must be reckoned with the "fixed tanning matters." The sum of the weights of dry residue, fats, and moisture should equal that of the leather taken. It is not usually necessary to dry the leather before extraction, and at least the drying should not be prolonged or at a high temperature, lest the oils become oxidised. In many cases a considerable percentage of fats is contained even in rough or uncurried leathers, either naturally or from added oil. The writer found 24 per cent. in a rough and apparently quite dry "Persian" sheep-skin.

When necessary more detailed examination of the fats may be made by the methods in Section XX., but the analysis is often limited by the small quantity of material available. Even on very small quantities the specific gravity may be determined by floating a globule in dilute alcohol (p. 291), the melting and solidifying points by the capillary-tube method (p. 291), and the refractive index by the butter refractometer. It is generally desirable to determine the acid and saponification values on the same quantity of fat, using alcoholic potash for the former, and then adding the usual 25 c.c. and saponifying (p. 304). The unsaponifiable matter may also be determined on the same portion by adding sodium carbonate till the titrated liquid is reddened, boiling slightly to insure the absence of traces of free fatty acids, diluting with water and shaking out with petroleum ether (p. 309). If the saponification has been done in duplicate, which, where the quantity of fat is sufficient, should always be the case, it is best to unite the two soap solutions before shaking out. The free fatty acids may now be isolated in the usual way, and their physical characteristics and iodine value determined. It must be borne in mind that all the constants are much influenced by oxidation.

Determination of Water-soluble Matter (Auswaschverlust).—
The dry leather residue from the Soxhlet is digested for some

hours with about 200 c.c. of distilled water at 15° – 20° C., and the whole is transferred to a syphon or Koch's extractor (p. 184), and extracted precisely in the same manner as a tanning material. If the leather has not been thoroughly ground, it is well to bruise it in the moist state in a clean mortar before transferring it to the extractor. The extraction is made at laboratory temperature, and the last washings are concentrated by boiling, so as to bring the whole within 1 liter, to which volume it is made up after cooling. Twice 50 c.c. of the filtered solution is evaporated and dried at 100° – 105° C. to determine the "total soluble." Soluble mineral ash may be determined by ignition of the residues.

Some chemists prefer to make the extraction at 40° – 50° C., instead of at laboratory temperature, and the question of which is preferable will depend largely on the purpose for which the leather is intended. Sole leather is never likely to be submitted to elevated temperatures, and it is therefore fairest to make the extraction at 15° – 20° C.; while in the case of rough dressing leather, which will be scoured out of hot water, the higher temperature may be preferred. It must be remembered, however, that at this temperature, a portion of difficultly soluble tannins will be dissolved, which will precipitate on cooling, and if the liquid is filtered before evaporating for "total solubles," a portion of matter will be removed which will be included neither in the solubles nor in the dry insoluble residue. Extraction at a boiling temperature, which has been proposed by some American chemists, is totally unsuitable, as the leather itself is partially decomposed.

The estimation of "uncombined tannin" is made by the hide-powder method, preferably, as described on p. 214. If the solution is very dilute it may be necessary to concentrate by evaporation before detannising, and this may be combined with the evaporation for glucose determination (see below). The nature of the tanning material may sometimes be determined by qualitative tests (Section IX.).

In the case of sole leathers or other rough leathers which contain no added fat, it may be convenient to determine the "water-soluble" before making the fat extraction, or even to omit the latter altogether. If the "water-soluble" determination is to be succeeded by a fat-extraction, it is necessary to dry the

extracted leather at a low temperature, especially at first, and the temperature should at no time exceed 50°C . The drying is best done in a draught of cool air, without using the drying oven, and the water estimation made on a separate portion, the residue being only finally dried at 100°C . and weighed after the fat extraction. By adopting this course the danger of rendering tannins insoluble by the production of anhydrides is avoided, but the additional drying slightly increases the trouble.

Estimation of Glucose and Dextrine.—400 c.c. of the water-extract is evaporated to 200 c.c., and the glucose estimation is made precisely as described on p. 270. Dextrines are determined as on p. 274. It must be borne in mind that all these sugar determinations refer to anhydrous glucose, while the commercial article contains 9 to 15 per cent. of water, and it may be fairly assumed that in the leather it retains at least as much water as the other constituents. The amount of glucose found by Simand's method should therefore be increased by the same percentage of moisture as that found in the leather. Tanning materials naturally contain glucoses and dextrinoid bodies (p. 276), and therefore small quantities are contained even in unweighted leathers. 2 per cent. is usually a sufficient allowance for glucose thus present, though it is said that leathers largely tanned with myrobalans may contain as much as 3 per cent., but this figure probably needs confirmation. Simand found that unweighted mixed tannages of oak bark, valonia, pine bark, etc., contained from 0.60 to 1.70 of sugar after inversion with acid, while that tanned with quebracho ranged from 0.22 to 0.35 per cent.

Von Schroeder gives the following table, which, however, refers to Continental tannages with relatively weak liquors, and is probably hardly applicable to present day methods.

Glucoses contained in various German Leathers :—*

	Per cent.
Heavy sole leathers, oak, pine-bark and mixed	0.11 to 0.41
Light sole leathers (<i>vache</i>)	0.40 to 0.53
Dressing and light leathers, calf, etc.	0.00 to 0.24

The glucose is largely proportional to the water-soluble matter present, which in the highest case was only 9.7 per cent. In English leathers it is usually much higher.

Von Schroeder, *Gerberei-Chemie*, pp. 552-55.

Commercial glucose always contains unconverted dextrine and dextrinoid bodies, and to estimate the total weighting, these must be converted into sugars by digestion with acid, as described on p. 274, before making the sugar determination.

If it be desired to determine the *insoluble residue* directly, sand must not be used in the extractor, and unless the leather is very finely ground, may generally be dispensed with, especially if the first portions of the filtrate be returned to the extractor so long as they contain traces of leather fibre. In this case the insoluble residue may be dried and weighed direct, and then incinerated to determine insoluble mineral matter, or a portion may be kjeldahled (p. 65), to determine the actual hide-fibre present; but in most cases it will be more convenient and quite as accurate to make the Kjeldahl determination on a separate portion of the original leather. Complete analysis of the insoluble mineral constituents is sometimes necessary, and the ash may then be examined as on p. 363. It is, however, usually sufficient to ascertain merely the proportion of ash from the soluble and insoluble portions, which should be approximately equal in sum to the total ash obtained by igniting a separate portion of the leather, which may be analysed in greater detail. If any considerable portion of soluble salts be present, the leather should be charred and extracted with water, as described below, before complete ignition.

It occasionally happens, both in vegetable and mineral tannages, that the whole of the gelatin is not rendered insoluble, but that a portion can be extracted by boiling. Drying at 100° C., however, renders gelatinous fibre very insoluble, even in boiling water, and it is better to treat a portion of the leather which had not been dried at a high temperature first with warm water to remove soluble matter, and then to boil it, and to test the solution with tannin for gelatin. There is no very satisfactory way of determining the amount quantitatively, but, of course the residue might be kjeldahled after evaporation to small bulk or to dryness. On the whole more valuable results are obtained by kjeldahling the leather direct, and so obtaining the relative proportion of nitrogenous matter (hide-fibre) to non-nitrogenous (tannins, fats, etc.). In heavily tanned leathers the latter often exceed the actual hide-fibre. If the boiling test is applied, it must be remembered that modern leathers may easily contain

an excess of soluble tannin and yet be imperfectly tanned in the centre or through the fibres.

The Total Ash should be obtained by igniting a separate quantity of the leather, which may vary in weight, according to the nature of the leather and the extent of detail which is required in the ash analysis. As leather melts and swells extremely in the early stages of combustion, it is best to heat a platinum* or porcelain basin to redness in a draught-chamber, and to throw in the weighed quantity of leather piece by piece, allowing time for the first portions to swell and carbonise before adding more. It is not necessary, or even advantageous, that the leather should be finely divided before incineration. As a general rule there will be little fusible matter, and the carbon will be easily and completely burnt without using a temperature above a dull red heat. Higher temperatures render the alumina, ferric and chrome oxides extremely insoluble, and may drive off chlorides and other salts which are slightly volatile. If a muffle is available it is probably the safest means of incineration. In the case of white leathers, or where soluble salts have been used for weighting purposes, and the carbon burns off badly, it is best to powder the charred cinder in a glass mortar, and extract it with a little boiling water on a quantitative filter. The insoluble residue is dried with the filter, and is now easily burnt to ash, and the solution is afterwards evaporated and the residue ignited in the same crucible. This is specially important in presence of sulphates, which are readily reduced to sulphides and even to carbonates by ignition with carbonaceous matter.

The ashes of natural rough leather are very small, amounting seldom to more than 2 per cent. in sole leather, and considerably less in dressing leather. They consist principally of calcium carbonate, with traces, which are usually negligible, of iron and phosphates. Finished and weighted leather, or that of mixed or mineral tannages, usually gives considerably larger amounts of ash of very varied composition, so that it is always best to make a preliminary qualitative examination. Lead is generally only found in leathers which have been "bleached" by the precipitation of lead sulphate on the fibre. It may be detected by the darkening of the leather or ash with hydric sulphide. Tin (as stannous chloride) is occasionally used to brighten dull-

* Before using platinum the absence of reducible metals must be ascertained.

coloured leather, or as a mordant for dye-woods, though for the latter it has been a good deal superseded by direct-dyeing aniline colours. Leathers containing either of these metals must not be ignited in platinum vessels. Titanium, in the form of lactate, oxalate, and sulphate, has latterly been used a good deal as a mordant for dye-woods, especially on chrome goods, and produces a good yellow with many tannins. It has also tanning properties. Copper, iron, aluminium, chromium, barium, calcium, magnesium, sodium, and potassium are all possible constituents of a leather ash, though not all likely to be present simultaneously.

Analysis of Leather Ash.—From the large variety of bases possibly present in leather ashes of various sorts, due to the tanning agents employed, the materials added for weighting purposes, and the mordants and pigments employed for dyeing, a complete general analytical scheme would prove extremely complicated, and is usually unnecessary, since many conclusions as to possible constituents can be drawn from the character of the leather; and the analysis is usually made with some particular object, such as the determination of the method of tanning, the detection of weighting or of free mineral acid, or investigation of materials used in dyeing. A preliminary qualitative examination is therefore very important, and in most cases greatly simplifies the quantitative work. It is not necessary here to specify a scheme for qualitative analysis, which does not differ from that employed in ordinary inorganic analysis, and for which the reader may therefore be referred to chemical text-books, but a few hints as to the detection of special substances may be allowed. Traces of chromium are easily detected by the deep green coloration given by the ash to the borax bead in the reducing flame of the blowpipe or Bunsen burner,* and alumina may be recognised in "crown," "rawhide," and other white leathers by the

Other metals give the following reactions in the borax bead :—

	Oxidising.	Reducing.
Iron . . .	Yellow, paler on cooling	Pale green
Copper . . .	Green, blue on cooling	Red
Manganese . . .	Amethyst red	Colourless
Nickel . . .	As iron	
Titanium . . .	Colourless	Yellow, cools violet

The titanium reaction succeeds better with ammonium-sodium phosphate than borax. In presence of iron, the bead is red.

violet-blue coloration given by an alcoholic extract of logwood diluted with water and applied to the leather. It must not be forgotten that reddish purples are given with logwood by alkalies and alkaline earths, and sometimes mask the colour produced by alumina. Violet-blacks are also produced by iron and chromium.

Baryta in any form is easily detected, and in many cases quantitatively separated by digestion of the ash with somewhat diluted sulphuric acid, which dissolves all other substances likely to be present except lead and strongly ignited chrome-oxide, and possible traces of tin. 1 grm. of ash may be digested for some hours on the water-bath with 4 c.c. of concentrated acid and 1 c.c. of water, and in absence of other impurities the mixture may be diluted with 25 c.c. of water; the baryta filtered off and washed, and finally ignited and weighed. Ground heavy spar (barytes) may generally be distinguished from precipitated barium sulphate by the coarser and sandy character of the precipitate. Lead, if present, may be removed by repeated boiling with ammoniacal solution of ammonium acetate, and chromium may be converted into a soluble chromate by ignition till pure yellow with sodium carbonate and magnesia (p. 265), or a mixture of sodium carbonate and peroxide, or, less satisfactorily, with four times its weight of Na_2CO_3 and twice its weight of KNO_3 for half an hour in a platinum crucible (which the mixture slightly attacks). In either case the soluble chromate is first removed by thorough washing with hot water, and the barium is then reconverted into sulphate (and magnesia removed if present) by treatment with dilute sulphuric acid, and subsequent washing.

In the ordinary qualitative analysis, tin should be looked for in the second (sulphydric) group, especially if the precipitate be yellow. It is separated from lead by boiling with yellow ammonium sulphide, in which it (together with As and Sb) is soluble. The separation of Sn from As and Sb together is difficult, but if a mixture of arsenic and tin sulphides are ignited in a tube in a current of SH_2 , the arsenic is completely volatilised. The arsenic sulphide may be condensed or carried into a good draught. Tungsten and vanadium are found in the same group as tin and arsenic.

Titanium, though by no means a rare metal, has only recently become of commercial importance, and is hence usually omitted

from the simpler schemes for qualitative analysis. Particulars as to its character, detection, and estimation will be found in the larger chemical text-books; but it may be mentioned here that it is precipitated by ammonia along with the iron, chromium, and aluminium group, from which it can be separated by solution in hydrochloric acid, careful neutralisation with ammonia till slight cloudiness is produced, and addition of dilute (say N/10) HCl drop by drop till the solution is again clear, when it is saturated with sulphurous acid and boiled, and TiO_2 is precipitated, the other bases remaining in solution. The filtered solution must be acidified with HCl, boiled to expel sulphurous acid, and the iron oxidised to the ferric state with nitric acid or bromine before proceeding to further wet separations. The separation of titanium is quantitative, and the TiO_2 may be ignited and weighed.

Alumina, when present, as is often the case, in small quantities with iron or chromium, is somewhat difficult to detect. On the whole the best method is to fuse the bases of the group with sodium carbonate, with small additions of an oxidising agent, such as sodium peroxide, and dissolve the melt in water. Ferric oxide will remain undissolved, chromium will dissolve as yellow chromate (see p. 253), and aluminium as aluminate, which may be precipitated by neutralisation with hydrochloric acid, and subsequent boiling with slight excess of ammonia. The separation is quantitative. Manganese, if present, will be recognised by the production of green manganate, which will turn pink on acidification with sulphuric acid. Other bases of the group, except perhaps zinc, are so improbable that they need hardly be looked for. Phosphoric acid is usually present in traces, and will come down with the group, either in combination with the bases, or, in their absence, as calcium phosphate. The quantity is so small that it may generally be disregarded.

The only other separation which is likely to prove troublesome is that of *magnesia* from the alkalies, which is often important in cases of weighting with magnesium and sodium sulphates. In most cases the solution of the last group, containing magnesia and the alkalies, is acidified with sulphuric acid, evaporated to dryness, and gently ignited to drive off ammonium salts and excess of sulphuric acid, small quantities of ammonium carbonate being added at the finish to decompose bisulphates. The whole

is then weighed as mixed sulphates, and the magnesia determined as pyrophosphate (p. 45), calculated to sulphate, and deducted. Where the quantities are small, the method of volumetric determination with barium hydrate, described on p. 45, is sometimes advantageous.

Qualitatively, magnesia is easily detected by the sodium phosphate reaction, but it is difficult to prove the presence of material quantities of soda, as the flame reaction is too delicate to be of much use. Mg may be precipitated by $\text{Ba}(\text{OH})_2$, filtered off, excess of $\text{Ba}(\text{OH})_2$ removed by passing CO_2 and boiling, and NaOH detected by its *powerful* reaction with phenolphthalein or litmus, or by evaporation, when it may be weighed as carbonate. In calculating loading with these salts, their water of crystallisation must not be overlooked.

Examination for Acids.—The examination for acids, and especially for free mineral acids, has become of great practical importance, especially since it has been shown that the decay of bookbinding and furniture leathers is largely due to the presence of small quantities of sulphuric acid. Much information on this point has been collected by the Committee of the Society of Arts which was appointed in 1890 to investigate this subject.* Most governments also demand freedom from sulphuric acid in leathers employed for military purposes. The determination of total mineral acids is also of great theoretical importance in the manufacture of chrome and other mineral leathers, with regard to the nature of the actual tanning salts which they contain.

Leather ash is practically always alkaline, and the salts present are mostly carbonates, arising from the destruction of organic alkaline salts, together with sulphates (and sulphides arising from their destruction by ignition in presence of organic matter), with possible traces of phosphates, silicates, and nitrites (from the destruction of nitrates). Sulphates of iron, chromium, and many other metals are more or less completely decomposed on ignition, leaving uncombined bases, and sulphuric acid in the form of ammonium salts is completely expelled. Qualitatively, all these may be tested for in the usual manner; organic acids must of course be looked for, if necessary, in the aqueous or alcoholic extracts of the leather.

* Society of Arts Report on Bookbinding Leathers, S.A. Journal, 1901, and separate editions, 1901 and 1905.

Free Mineral Acids.—The detection, and still more the exact estimation of these is a matter of great difficulty, and the methods at present available* are not wholly satisfactory. Most leathers when moistened are acid to litmus, but this, unless extremely marked, is no evidence of the presence of free mineral acids, and it is rarely that definite indications can be obtained with methyl orange or Congo red, which are much less sensitive than litmus to organic acids, but of course a strong acid reaction, especially in the presence of much sulphate, is very suspicious. On the other hand, even if free sulphuric acid has been intentionally introduced into leather, the ash will usually prove to be alkaline, since the whole of the free acid is driven off in ignition, and a portion of the sulphates is reduced by the carbon to sulphides, and apparently these in their turn may be decomposed and converted into carbonates or free bases, especially in the case of lime. The investigation is greatly complicated by the fact that free mineral acids are very obstinately retained by leather, and sulphuric acid especially probably exists to a large extent in the form of organic compounds insoluble in water or alcohol, which may or may not exercise a destructive action.

In consequence of the facts just mentioned, no method has been, or probably can be devised for the direct removal and estimation of the free sulphuric acid from leather. The most satisfactory method of this sort is that of Jean,* who extracts the dry leather with absolute alcohol in the Soxhlet apparatus, a little sodium carbonate being placed in the boiling flask to combine with any sulphuric acid dissolved. On distilling off the alcohol, any free acid remains as sulphate, and may be estimated as barium sulphate, if necessary after partial ignition to destroy organic matter. Care is required that the alcohol is really absolute, as the accuracy depends on the fact that free sulphuric acid is soluble in absolute alcohol, while sulphates are left undissolved. For the same reason, the leather should be dry, but extreme drying, and especially the use of high temperatures, should be avoided, lest the acid should attack and combine with the organic constituents of the leather. A positive result may be taken as absolute proof of the presence of free acid, but, from reasons already given, a negative one is no evidence that acid is

* *Revue Chim. Analyt.*, 1895, pp. 3 and 13.

not present, even in injurious quantities, since tests with added acid show that the extraction is far from complete.

Another group of methods, among which may be mentioned that of Balland and Maljean* with its modifications by Paessler and Sluyter†, Meunier‡, and others, and of Procter and Searle§, depend on the fact that while free sulphuric and hydrochloric acids are expelled by ignition, they are converted into sulphates and retained when the ignition takes place in presence of alkaline carbonates. All these methods suffer from the common defect that sulphates are easily reduced to sulphides, and even to oxides and carbonates by ignition in presence of organic matter, and most of the proposed modifications have been directed to minimise this evil. Probably the most accurate methods are those of Stiasny|| and Wuensch,¶ in which the organic matter is oxidised with fuming nitric acid. In all these oxidation methods the sulphur naturally present in the skin is more or less perfectly oxidised into sulphates, and must be allowed for in calculating the results. Its quantity is rather variable, and would be influenced by sulphates present in the waters employed in manufacture. Paessler and Sluyter,** working by Balland and Maljean's method, found in seven sole-leathers, tanned without acid, quantities varying from 0.115 to 0.173 per cent., with an average of 0.140 calculated as SO_3 on leather with 18 per cent. of water. On *dry* leather the mean would be 0.170 per cent. Balland and Maljean themselves operating on eighteen leathers, mostly French, found from 0.025 to 0.086, with a mean of 0.058 per cent. on dry leather. The French leathers were tanned by the old method, and unhaired by sweating. On the dry substance of fresh hides unhaired with lime, the same chemists found from 0.126 to 0.169; when unhaired with sulphides, from 0.138 to 0.561 all reckoned as SO_3 . It is therefore clear that this figure is sufficiently variable. Meunier, employing a more complete oxida-

* Revue de l'Intendance, 1894, p. 380; Annales de Chimie Analytique, 1904, Sept. 15; Collegium, 1904, p. 389.

† Deutsche Gerber-Zeitung, 1901, Nos. 66 and 69; Wiss. Beilage des Ledermarkt, 1901, p. 133.

‡ Collegium, 1906, pp. 13 and 296.

§ Lea. Trades Rev., 1901, Jan. 9; Wiss. Beilage, 1901, p. 65.

|| Gerber, 1901, p. 235.

¶ Wiss. Beilage, 1901, p. 147.

** Loc. cit.

tion method,* found much higher figures. In a non-acid French leather from St. Saens in six determinations, his result varied from 0.204 to 0.296 per cent., while Balland only found an average of 0.077 of SO_3 in leathers from the same place. It is pointed out by Balland that very small quantities of the hair or hair-roots retained in the leather will largely influence the results, hair containing from 2 to 3 per cent. at least of S reckoned as SO_3 . It is therefore probably not worth while to go to great refinements in oxidation methods till this source of uncertainty can be removed.

The simplest, and by far the most rapid oxidation method is that of Procter and Searle,† which will rarely mislead if properly carried out, though it tends to give results lower, rather than higher than the truth, while the opposite is the case with the method of Balland and Maljean, in which destruction of sulphates is certain to occur in the ignition in absence of alkali. For the determination, 2 to 3 grm. of the leather are moistened in a platinum basin or crucible with 25 c.c. of accurately standardised and measured N/10 sodium carbonate solution, and after evaporation to dryness, the mixture is charred at a gentle heat till thoroughly carbonised. Under these conditions much if not all the organic sulphur escapes as volatile compounds, while the reduction of sulphates is very slight. The carbonaceous mass is pulverised with a glass rod, and extracted with boiling water, and the solution filtered through a small ashless filter paper, which is dried and returned to the mass in the crucible, and the whole is ignited till all, or nearly all carbon has disappeared. The crucible is now cooled, and the ash treated with 25 c.c. of N/10 hydrochloric acid, accurately standardised to the soda, to dissolve any calcium carbonate present, and the whole is washed into a beaker with the filtrate of the charred mass, methyl orange is added, and if the liquid shows an acid reaction it is titrated with N/10 alkali, and the amount calculated as mineral acid, generally sulphuric. If the reaction is alkaline, sulphuric acid is absent, and no notice need be taken of the alkalinity. It does not seem necessary in this case to make any allowance for sulphur naturally present in the hide, as probably most of the organic sulphur is distilled off in charring, and any sulphuric acid formed in this way may be set against possible losses by oxidation. The sulphuric

Collegium, 1906, p. 298.

Loc. cit.

acid of ammonium sulphate, and of iron, chromium, and aluminium sulphates will be reckoned wholly as free sulphuric acid, since the ammonium sulphate will escape, and alumina, and iron and chromium oxides will be rendered too insoluble to be taken up by the dilute standard acid. These errors are common to all ignition methods. Of course in all such determinations care must be taken in ignition to avoid contamination with sulphur from gas-flames, and it is safer to use an alcohol or petroleum burner, or carbonise in a muffle.

The method of Baland and Maljean is carried out as follows : 2 to 5 grm. of the leather are moistened with excess of potassium or sodium carbonate, dried, and slowly ignited at as low a temperature as possible, care being taken to allow free access of air. The residue is dissolved in hydrochloric acid, filtered if necessary, and the sulphuric acid is estimated gravimetrically with barium chloride in the usual way. A similar quantity of the leather sample is ignited in the same way, but without addition of alkali, and the sulphuric acid again estimated. In theory the first estimation gives the total sulphuric acid present, both as sulphates and free acid, while the second gives that present as sulphates only ; and deducting this from the first, the free sulphuric acid is found. The sulphuric acid due to sulphur in the leather is deducted from this (see above) ; and as published results are very variable, and the method is liable to errors, it is perhaps best determined on samples known to be free from added acid by the same method as is used in the estimations. Apart from this source of error which is common to all oxidation methods, the principal cause of inaccuracy is the reduction of sulphates by the carbon, sodium sulphate being reduced to sulphide, and in presence of lime salts to carbonate, and a part of the sulphur seems actually to be expelled and lost. It also seems that some of the organic sulphur is distilled and burnt outside the alkaline mass, as Meunier,* igniting in a current of air, was able to collect sulphuric acid among the volatile products. Paessler and Sluyter oxidise the dissolved products by addition of bromine water, but this, though it lessens, does not avoid the error. Meunier found the oxidation improved, but not made complete by the use of a mixture of nitrate of potash and caustic potash for moistening before ignition. He finds that correct results, so far as oxidation is

* Collegium, 1906, p. 16.

concerned, may be obtained by combustion in a tube in a current of oxygen with addition of nitrated lime, a reagent proposed by Nihoul and Koninck, but the process is somewhat troublesome, and the large quantity of calcium salts introduced involves great care in the estimation of sulphuric acid. He obtains good results by combustion in oxygen at a pressure of 30 atmospheres in a Mahler's bomb, such as is used for calorimetric determinations. None of these improvements, however, prevent the possibility of loss of sulphates in the ignition in air to drive off the free sulphuric acid, and the tendency of the method is therefore to obtain too high results. M. C. and J. W. Lamb,* acting on a suggestion of Procter's, ignite the untreated leather by heating gently till the greater part of the volatile matter is driven off, placing the hot crucible in a soup plate to avoid possible loss of ash, and passing in oxygen through a tube passed through a suitable perforated cover. A sheet of asbestos cardboard with a hole for the admission of the tube, or an inverted funnel, may be used. The mass glows, and the combustion is nearly complete without further heating. They also describe a further method in which the leather is dissolved in caustic soda, the solution acidified, and the organic precipitate caused by acidification well washed, and sulphuric acid determined in the filtrate with benzidine hydrochloride (see p. 47). A similar determination is made of sulphates in the leather ash, and deduction of this from the first determination gives the free acid. The method is stated to be accurate, and seems to deserve further examination.

Probably the most accurate method at present known, though somewhat troublesome, is that of Wuensch,† which is almost identical with one proposed by Stiasny‡ for the estimation of acids in chrome leather, which will be described more fully below. The finely cut leather (about 5 grm.) is dropped shred by shred into fuming nitric acid (50 c.c.), in which it is rapidly and completely oxidised, at first usually with actual combustion. If sulphuric acid only is in question, heat may be used towards the end of the operation to complete the oxidation and solution, but if hydrochloric acid is to be estimated, the operation must take place in the cold, which will require twelve to twenty-four

* Collegium, 1904, p. 25.

† Wiss. Beilage, 1901, p. 144.

‡ Gerber, 1901, p. 236.

hours for complete solution. The nitric acid must be of S.G. 1.52, and free from sulphuric acid or chlorine. When only sulphuric acid is to be estimated, Wuensch evaporates the green solution with some barium chloride and hydrochloric acid to dryness to drive off nitric acid, filters, and washes the residue with dilute hydrochloric acid, and after ignition weighs as barium sulphate. The filtrate is now treated with sulphuric acid to remove barium and convert all bases into sulphates. After filtration to remove the separated barium sulphate, the solution and washings are evaporated to dryness, ignited, and smoked off with ammonium carbonate to decompose bisulphates, and after acidification with hydrochloric acid, the sulphuric acid is determined with barium chloride in the usual way, and represents the total sulphuric acid which the bases are capable of neutralising. If the first determination exceeds the second, the difference represents free sulphuric acid in the leather; if on the other hand the acid combined with the bases is the greater, the excess represents bases uncombined with sulphuric acid, and no free sulphuric acid can be present. With regard to this method it may be remarked that difficulties sometimes arise from the "puffing" of organic nitro-compounds in the ignition of the evaporated filtrate; and that while the method is accurate with alkaline and alkaline-earth bases, sulphuric acid would be expelled from ferric or chromic sulphates, and ammonium sulphate would be driven off. If it be desired to estimate chlorides as well as sulphates, the oxidation must be conducted in the cold, and barium nitrate and silver nitrate added to the solution before evaporation, and the residue washed with hot water instead of dilute hydrochloric acid. The precipitate containing silver chloride and barium sulphate is treated with ammonia to dissolve out the silver chloride, the barium sulphate is filtered off, ignited and weighed; and the silver chloride is estimated in the ammoniacal solution, probably most easily by boiling off the excess of ammonia, and precipitating by neutralising with acetic acid. The total bases are determined as sulphates in the filtrate as before after freeing it from both silver and baryta by sulphuric and hydrochloric acids, and a proportion reckoned into chlorides corresponding to the chlorides found.

Stiasny,* in his method for the examination of chrome

* *Loc. cit.*

leathers, requires only the *total* sulphates and chlorides, and hence proceeds somewhat differently. Two-bath and other leathers containing free sulphur are first carefully extracted in the Soxhlet with carbon disulphide. The residue in the flask gives the sum of sulphur and fats, in which the sulphur can be estimated as sulphuric acid after oxidation with nitric acid. The extracted leather is dried for a long time at 110° C. to remove all traces of carbon disulphide, and is then dissolved in fuming nitric acid as above described (by digestion in the cold if chlorine is present). The green solution is poured into 400 c.c. of cold water contained in a large beaker surrounded with cold water to prevent rise of temperature. The solution is made up to 500 c.c. 100 c.c. is treated with silver nitrate, and after heating to complete subsidence the silver chloride is collected in a Gooch's crucible, ignited, and weighed. A second 100 c.c. is evaporated to dryness to drive off excess of nitric acid, and after taking up with water, the sulphuric acid is estimated with barium chloride. 200 c.c. is evaporated to small bulk in a porcelain basin, and finally to dryness in platinum, and *gently* ignited to destroy organic matter; the residue is extracted with dilute hydrochloric acid to remove alkaline bases; any dissolved chrome oxide is precipitated with ammonia, filtered off and added to the insoluble, and the whole is fused with sodium carbonate and magnesia, and the chrome estimated with potassium iodide and thiosulphate (Procter's method, p. 258). If it is not desired to estimate other bases than chromium, there seems no reason why the evaporated and ignited residue should not be moistened slightly, and mixed at once with the sodium carbonate and magnesia mixture. The method is much more accurate than direct incineration of the leather and examination of the ash, as the ignition always involves loss of acids.

SECTION XXIII.

DYES AND DYESTUFFS.

IN leather-dyeing, coal-tar colours have to so large an extent superseded the natural dyestuffs, that no apology is needed for giving them the first place. It is needless to say that these colours are not in any ordinary sense "extracted" from coal-tar, but are chemical derivatives and compounds, mainly from the three hydrocarbons, benzene, naphthalene, and anthracene; of which tar is the cheapest and most abundant, but by no means the only source. It may be said, in general terms, that the aniline and phenol dyes are derivatives of benzene and its homologues, and the alizarine colours those of anthracene; while naphthazarin is a corresponding naphthalene derivative; but the colour molecules are usually extremely complex, and often contain molecular groups from more than one of these types, and are therefore not susceptible of any simple classification on these lines. The statement should not be omitted that the introduction of nitrogen in very varied modes of combination plays a most important part in the production of colouring matters. It is obvious, from what has just been said, that these colour compounds are so numerous and complex, and their number is so constantly being added to, that they can only be treated here in general terms, and that no complete scheme of analysis or recognition can be given. The question is not simplified by the fact that the ordinary names of the colours are chosen by their respective makers, and bear no relation to their chemical structure; so that in many cases identical or nearly identical compounds are known by different names, while in others the same name is made by different makers to serve for colours similar in tint, but of widely different chemical nature and dyeing properties.

In practice, therefore, we may wish to determine whether two dyes by different makers are identical, or at least so closely allied that they may be expected to dye in the same way, or in the same bath; or to determine what materials have been used in dyeing a special leather sample; or, on the other hand, we may

desire to know whether some familiar colour is of full strength and true shade. In the latter case, we shall probably resort to laboratory dyeing trials, while in the former, more strictly chemical means must be employed.

Many methods of classification and identification have been suggested, among which may be mentioned that of Weingartner as improved by Green.* This, however, even when published, left something to be desired as a means either of classification or recognition, and with the multiplication of dyes has become quite out-of-date, and though Professor Green is engaged in remodelling it the work proves by no means easy and is not yet complete, and the Tables are therefore omitted in the present edition. We have thus to be content in general with practical trials and a few unsystematic tests, which, while they are often enough to establish the identity or close relationship of two dyes, tell but little about their constitution.

Probably the most important division of the coal-tar colours for the practical dyer is that into "basic" and "acid" colours. The basic dyes are complicated compound ammonias, generally insoluble in water in the free state, but often forming soluble salts, such as chlorides and acetates, which form the commercial dyes. Thus "fuchsin" or "magenta" is rosaniline chloride or acetate; "chrysoidine" is diamido-azobenzene chloride. With temporary-hard waters containing carbonates of lime and magnesia, these salts are decomposed and the free bases precipitated, causing waste of colour and irregular dyeing, hence the importance of neutralising alkaline waters with a weak acid such as acetic. Strong acids, or even acetic acid in considerable excess on the other hand, check or prevent dyeing by rendering the salt too stable to be decomposed by the fibre. All basic dyes are precipitated by tannins, and thus are easily fixed on leather and tanned cotton, but are thrown out of solution by any excess of soluble tannin. For this reason, leather to be dyed by basic colours must either be thoroughly freed from loose tannin by washing, or the excess of tannin must be fixed by treatment with some metallic salt, such as tartar emetic, the metallic tannin compound being still capable of fixing basic colours. A convenient reagent for basic colours is a solution of 10 per cent. of tannin and 10 per cent. of sodium acetate in water, by which all

* Journ. Soc. Chem. Ind., 1893, p. 3.

basic colours are precipitated, while "acid" dyes remain in solution.

The "acid" dyestuffs are colour-acids, and appear in commerce as salts in combination with bases such as sodium, magnesium, and occasionally other metals. They are not precipitated by tannins, and usually dye best in acid solution. For acidification, sulphuric acid is generally employed, but in view of its destructive action on leather, formic should be substituted in the dyeing of all leathers where permanence is important. If sulphuric acid is used, it should only be employed in the very small quantity required to neutralise the base, and set free the colour-acid. Kauschke* states that one-fourth the weight of the colour employed is in all cases sufficient. Naturally, with hard waters, the calcium carbonate must also be neutralised.

Some few colours, and especially the nitro-colours, are acid in their nature: picric acid (trinitrophenol), for instance, has strongly acid properties, easily decomposing carbonates, and forming stable salts; but in many cases colours are made acid by sulphonation, often for the purpose of increasing their solubility, or enabling them to be used in mixture with other acid dyes, many of which precipitate basic dyes. Sulphonation consists in treating the dyestuff, which may be basic or neutral, with concentrated sulphuric acid or sulphuric anhydride, which introduces the SO_3H group in place of a hydrogen atom of the compound, which (where sulphuric acid is used) combines with one OH of the acid to form water. The addition of this group, without generally much altering the colour, gives the dyestuff a strongly acid character, and the salts which it forms are usually soluble in water, and no longer precipitated by tannin, but generally dye leather without a mordant, though the colour intensity is usually somewhat less than that of the original basic dyestuff.

It is, perhaps, desirable, before proceeding further, to give a very slight sketch of the constitution of the principal groups of artificial dyestuffs, assuming on the part of the reader some knowledge of structural organic chemistry, and especially that of the benzene derivatives, of which a sketch has already been given in connexion with the chemistry of tannins (p. 105). The benzene group of six carbon atoms occurs so frequently

* Collegium, 1906, p. 357.

that it is usually represented by a simple hexagon $\langle \rangle$, and it is understood that each angle represents a carbon atom combined with a single atom of hydrogen, unless other connexions are shown: thus $\langle \rangle\text{NO}_2$ represents nitro-benzene, $\text{C}_6\text{H}_5\text{NO}_2$. Nitro-benzene is easily produced by the direct action of nitric acid on benzene, and is the oily "oil of mirbane," often used as a substitute for almond-flavouring. When nitro-benzene is treated with nascent hydrogen, produced, say, by a mixture of zinc dust and a dilute acid, the two atoms of oxygen are removed as 2OH_2 and replaced by H_2 , forming $\langle \rangle\text{NH}_2$, aniline or phenylamine, which may be viewed as a compound ammonia in which one of the H atoms is replaced by phenyl, C_6H_5 , or $\langle \rangle$. Such groups or "radicles" may also replace hydrogen in other compounds, and other atoms or groups may replace the remaining hydrogens of the benzene ring. The cause of colour in these compounds is not easily determined, but certain groups and arrangements of atoms, which probably result in a strained or unstable equilibrium, seem to produce it, probably by rendering vibration in unison with the light waves possible, while other groups, like the loading on the strings of a musical instrument, alter the tone, and consequently the colour of the light absorbed.

Nitro-Colours.—Probably the simplest class of artificial organic colours illustrate this point. Nitrobenzene is colourless or at most, pale yellow, while the addition of an OH group as in

1:2 nitrophenol $\langle \rangle^{\text{OH}}\text{NO}_2$ causes yellow coloration, while trinitrophenol or picric acid is primrose yellow, and to a certain extent used as a dye. Thus both the nitro and the OH groups are necessary to the development of colour in this case. The nitration of the naphthols produces still more powerful yellows, as Martius yellow, the soda (or other) salt of dinitro- α -naphthol

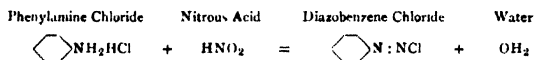


and naphthol yellow, a sulphonated derivative. The

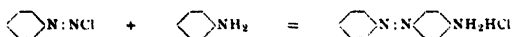
latter is the only nitro-colour now of importance, the others having gone out of use from their fugitiveness, and their poisonous and often explosive characters. It may be noted that while phenols such as "carbolic acid" possess no marked acid character, the nitro-phenols are strongly acid in character, and form well-defined salts.

Nitroso-colours form green lakes with iron, but are almost insoluble in water and not used for leather dyeing. They contain the group $-NO$ (or possibly $=NOH$) in place of the nitro-group.


Azo-colours are now one of the most important groups of artificial dyestuffs. They owe their name and probably their colouring power to the $-N:N-$ group which they contain, and which links together different parts of the molecule. If the salt of a primary amine, such as aniline (phenylamine), be treated with nitrous acid, the amido-group is attacked, the whole of its hydrogen being removed as water and replaced by nitrogen, thus



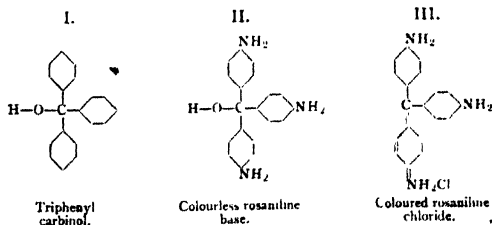
The reaction is generally performed in practice by adding the calculated quantities of hydrochloric acid and sodium nitrite to the solution of the amine chloride, which is kept cooled by ice. If the diazo-compound thus formed is treated with either an amine or a phenol, the two are linked by the azo-group, the Cl of the diazo-chloride uniting with the displaced H of the other to form HCl; the particular H displaced varying with the conditions of reaction, but being usually in the para-position to the amido- or hydroxylic group of the amine or phenol. Thus if diazobenzene chloride is mixed with aniline, the two unite forming aniline yellow—



As the aniline yellow contains an amido-group it can be again diazotised and coupled with a new phenol or amine, thus forming a new dyestuff containing 2 diazo-groups and hence styled a tetrazo-compound. When 2 diazo-groups are added in different positions to one phenol the compound is styled "disazo." "Amido-azo" compounds are those in which the diazo-compound is coupled to an amine; "oxyazo" those in which it is coupled to a phenol. As any primary aromatic amine can be diazotised, and coupled to almost any compound of an amido- or phenolic character, the number of possible azo-compounds, mostly dyestuffs, is practically unlimited; and among these the oxyazo dyes in which the naphthol-sulphonic acids take the part of the phenol, and which include the "croceins," "ponceaux" and

"fast reds," and many other most brilliant scarlets and oranges, are of special importance. Naphthalene, from which the naphthols are derived is a double benzene ring , and different naphthols and naphthol-sulphonic acids owe their distinguishing properties to the particular positions on the rings occupied by the OH and SO₃H groups respectively. The amido-azo dyes are naturally basic, but may be rendered acid by sulphonation, or acid dyes may be formed by the coupling of amido-sulphonic acids in the place of simple amines. They are however now of subordinate importance, except in the cases of chrysoidine and Bismarck brown, which are basic dyes, and of some sulphonated yellows and oranges, among which "methyl orange" may be named, which is prepared by coupling diazobenzene-sulphonic acid with dimethylaniline.

Triphenylmethane dyestuffs, of which rosaniline is an example, and which include some of the earliest of the coal-tar colours, form another very important section. They are all derivatives of triphenylmethane, which is methane, CH₄, in which 3 of the hydrogens are replaced by benzene rings. Perhaps more strictly they should be described as derivatives of triphenylmethane-carbinol, which is methyl alcohol CH₃OH in which the H₃ is replaced by three phenyl (C₆H₅-) groups, as in formula I. The free



para-rosaniline base, which is colourless, is shown in II., and the coloured chloride, the ordinary "magenta" of commerce, in III. The modern view is that the H of the HCl combines with the OH of the carbinol to form water, and the liberated bond of the methane carbon unites directly with the aniline-chloride ring, thus causing rearrangement of bonds shown in III. and allowing the N also to be doubly linked at the other side of the ring. This is the so-called "quinonoid" structure, which seems to be

one of the most important causes of the development of colour, and this change of structure on acidification is common to all of the basic triphenylmethane colours. Other rosanilines exist in which there are one or more CH_3 groups replacing H on the benzene rings, derived from the use of toluidine in the preparation. The presence of these methyl groups *on the ring* does not materially influence the colour.

If on the other hand methyl or ethyl groups replace H in the amido-groups, the colour becomes violet, of a bluer shade in proportion to the number introduced, the bluest methyl violet, 6B "crystal violet" having all 6 amido hydrogen atoms replaced by CH_3 .

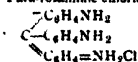
If in place of methyl, phenyl be introduced (by heating rosaniline with aniline in presence of benzoic or acetic acid) blues are produced ("victoria blue," "night blue," etc.). Most of these basic blues are insoluble in water, but are rendered acid and soluble by sulphonation ("Nicholson's blue," "cotton blue," "water blue").

If in the rosaniline molecule only two of the three benzene rings are amido, while the third is simply phenyl, green or blue instead of red colouring matters result. The best known of these are "malachite green" and "brilliant green" as basic dyes, and "Helvetia," "acid," and "fast green" as sulphonated derivatives.

Dyestuffs are also formed when phenols instead of amines form the triphenyl group, or in other words when OH takes the place of NH_2 . Of these, "aurine" (rosolic acid) is the simplest, but is no longer used as a dyestuff, but sometimes as an indicator. Rosolic acid is a yellow dyestuff, but on heating with ammonia, takes in an amido group (thus approaching rosaniline) and becomes red ("corallin").

Not very distantly related to the rosolic acid group are the phthaleins, with their derivatives fluorescein, the eosins, and rhodamines. These are now generally classed as "pyronine" dyestuffs, but in many cases at least, their formulae can be so written as to bring out strongly their resemblance to the triphenylmethane group, as is shown below—

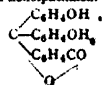
Para-rosaniline chloride



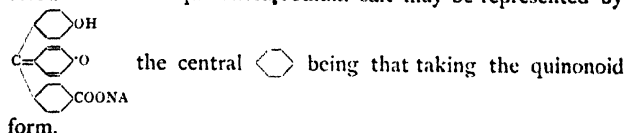
Rosolic acid



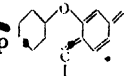
Phenolphthalein

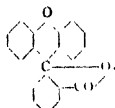


The formula of phenolphthalein just given is of a lactone type, and represents the colourless state. On the addition of a small quantity of alkali, it becomes brilliant red, and at the same time, according to Green and Perkin,* passes into the quinonoid form. On addition of a further quantity of alkali, this quinonoid state is again disturbed, and the salt becomes colourless. The quinonoid sodium salt may be represented by




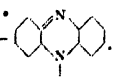
While the above formulae develop the relations of the phthaleins to triphenylmethane, their relation to the pyronine

group  is equally obvious. Phenolphthalein easily parts with a molecule of water from the two hydroxyls, and


then becomes . Phenolphthalein is formed by the con-


densation of ordinary phenol with phthalic anhydride $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown O \end{smallmatrix}$. If other phenols are substituted, other phthaleins are obtained. Resorcinol, for instance, yields fluorescein, which is the parent substance of most of the cosins, which are its iodine and bromine derivatives. The rhodamines are formed by the substitution of dialkyl (dimethyl, diethyl, diphenyl) amidophenols for the simple phenol employed in phenolphthalein.

Another group, the acridine dyestuffs, including phosphine, benzoflavine and acridine orange are somewhat similarly related,

but contain an N in the position . The safranines (including mauve, the earliest of the aniline colours) are basic dyestuffs, in which three benzene rings are linked together by two nitrogen atoms—.

* Trans. Chem. Soc., 1904, p. 398.

More important are the alizarine dyestuffs, derived from anthraquinone, , itself a derivative of anthracene. Ali-

zarine, , is identical with the natural colouring matter

of madder, the cultivation of which it has entirely superseded. Alizarine (Turkey red) is a mordant dyestuff, giving deep red with alumina, and violets and darker tints with other mordants; and its colours are remarkable for their fastness to light and washing. Many other anthraquinone derivatives, so-called "alizarine reds," "blues," "violets," and "oranges," possess similar characteristics of fastness and polygenetic dyeing.

The above brief summary must suffice. Some important groups and many important individuals have been unnoticed, but even a slight sketch of the whole subject would exceed the limits which can be allotted to it in this volume. Indigo, the most important of the natural dyestuffs, is an aniline derivative, and is now produced artificially on an extensive scale. The yellow natural dyestuffs associated with tannins have been briefly noticed on p. 141. Hæmatein, the colouring matter of logwood, is of a somewhat analogous character to these.

No simple and satisfactory tests are known by which the different groups described can be distinguished from each other. Most colouring matters can be decolorised by reduction with nascent hydrogen produced in acid or ammoniacal solutions by the addition of zinc dust, but the cause of decolorisation varies in different cases, the dyestuff being completely broken up in azo, nitro, and nitroso colours, while in many other cases, so-called leuco-derivatives are formed which either reoxidise with more or less rapidity on exposure to air, with return of colour, as in azine, and acridine colours, or only do so by treatment with an oxidising agent such as chromic acid, as in the triphenylmethane group. The return of colour, however, varies much in ease and rapidity, and in some dyes new colours are formed on reoxidisation. Green * says: "In the application of the zinc-dust reaction I have found that whilst the derivatives of triphenylmethane after reduction are reoxidised by air only with great difficulty, the azines,

oxazines, thiazines, and acridine colours all reappear with great rapidity on exposure of the reduced solutions to the atmosphere.

"On the other hand, the triphenylmethane colours are distinguished from those which do not yield leuco compounds, but are completely broken up, by the colour of the reduced solution being restored by chromic acid. The quinoline and primuline colours are distinguished from other dyestuffs by the great difficulty with which they are reduced, primuline for instance remaining unaltered after long boiling with zinc-dust and ammonia.

"The reduction with zinc-dust requires to be performed with some care. It is usually best to add a little zinc-dust to the hot solution of the colouring matter contained in a test tube, to agitate, and then add dilute hydrochloric acid drop by drop until decolorised. An excess of acid must be carefully avoided. In other cases, more especially when the colour-acid is very insoluble, the reduction must be performed with zinc-dust and ammonia; but it is usually safest to repeat the tests with both methods of reduction.

"Whilst it is important that the colouring matter should be completely reduced, care should also be taken that the reduction is not carried too far, for some colouring matters (e.g. the indulines) which usually form oxidisable leuco compounds are thereby completely altered. When reduced, the solution is poured off from the greater part of the zinc-dust on to a piece of white filter-paper, and exposed to the air; filtration is unnecessary, as a little zinc upon the paper has no injurious effect. If the colour does not return in a minute or two, the paper is touched with a glass rod dipped in a 1 per cent. solution of chromic acid (with addition of sulphuric acid for acid colours). Warming gently for a few seconds over a flame facilitates the reactions, and should also be employed when the reduction has been performed with zinc-dust and ammonia, in order to remove the excess of the latter before adding chromic acid, which would otherwise be neutralised.

"In the case of acid colouring matters, the paper, after spotting with chromic acid, should be held over a bottle of strong ammonia, for some acid colours (e.g. the eosines) do not show their true colour whilst acid. On reduction of those eosines which contain iodine, a brown spot of the latter is obtained with

chromic acid, but this disappears on exposure to ammonia vapour, and the original colour of the eosine (or a rather yellower shade) returns. As already pointed out by Weingärtner, great care must be taken that one is not led astray by secondary colours formed by oxidation of the diamines and amidophenols obtained by reduction of azo-colours."

A large number of dyes sold under special names, or supplied to produce particular tints, are merely mixtures of two or more well-known colours. Browns, for instance, frequently consist of Bismarck or some other common brown shaded by the addition of small quantities of benzaldehyde green or methyl violet. Such mixtures are often useful, though they not unfrequently dye unevenly from the different affinity of their constituent colours for the leather, and skilful dyers will usually prefer to mix for themselves. They are not easy to separate chemically, but may frequently be detected by sprinkling or blowing the powder very sparingly on a piece of wet filter paper, when the separate grains will give specks of different colour. In place of wet paper, the surface of water in a beaker may be sprinkled, and the threads of coloured solution watched from below. In some cases, where the mixed colours are too similar in appearance to be detected in this way, they are revealed by sprinkling in a shallow basin on concentrated sulphuric acid, in which many dyes dissolve with very different colours to those of their solutions in water (Spiller, Allen).

Another method, which is applicable to solutions of mixed dyes, is to place a drop on a sheet of filter paper, when, in case of mixtures, concentric circles of different colour will frequently be formed, because of the different diffusibility of the colours. Solid dyes are generally best dissolved in a small quantity of alcohol, and the solution diluted with its own volume of water. Goppelsroeder* suspends strips of Swedish filter paper with their lower ends dipping in small beakers containing the dye-liquors, and thus allows a more prolonged and complete diffusion. It must be remembered that in many cases the dyes, as manufactured, are not pure chemical products, but contain small proportions of other colouring matters produced at the same time by secondary reactions. Thus magenta often contains traces of phosphines.

* Journ. Soc. Dyers. etc., fv. p. 5.

Mixtures may often be detected by dye-tests, if the affinity of their constituents for the leather or textile fabric is at all unequal, since the first portions dyed in a bath will not only be darker in colour, but of different tint to the later ones, because those colours which have least affinity are left in larger proportion in the bath.

The use of the spectroscope will often detect differences in colouring matters of which the tint to the eye is identical. The dye is dissolved in water or alcohol, and diluted in a test-tube or small rectangular bottle till the absorption-bands appear to the greatest advantage when the light passing through the solution from the sky or a lamp is examined. A small pocket spectroscope is well adapted for the purpose, but it should be provided with a prism to permit the direct comparison of two solutions. The advantage of rectangular bottles over test-tubes is not only that the light passes better through the flat sides, but that two different thicknesses of solution are available by turning the bottle, and the appearance of the spectrum is often greatly influenced by the thickness or concentration of the solution. A very elaborate series of tables for the identification of artificial colouring matters by their absorption spectra has been published by Formánek,* but its use requires the employment of a spectroscope fitted with apparatus for measuring the position of the bands.

The analysis of curriers' inks and other blackings for leather is a problem which not unfrequently occurs to the leather trades chemist. The colouring matters of these inks are usually logwood or tannins (frequently with fustic or quercitron to destroy the bluish shade of the blacks) in combination with iron, and often with small quantities of chrome and copper salts, the chrome being added in the form of bichromate to oxidise the logwood and iron. Aniline colours may also be present. The separation of these different dyestuffs may sometimes be effected by the capillary method with strips of filter paper which has been described above, but is very difficult by any strictly chemical process. Logwood usually gives a red solution or residual colour when discharged by hydrochloric acid, while pure tannin blacks become yellow or colourless. By treatment with

* *Spektralanalytischer Nachweis künstlicher organischer Farbstoffe.* J. Formánek, Berlin, 1900.

caustic soda, a portion of the logwood colouring matter may be brought into solution in a colourless form, which turns violet on acidification. Gallic acid and the colouring matter of logwood can be separated in some cases by shaking the ink out with ether after acidification. If the ether be shaken with water and a little ammonia, logwood gives a pinkish violet coloration. Some aniline colours can be shaken out with amyl alcohol.

As a rule, the most useful information is obtained by examination of the ash obtained on incineration. Chromium is not likely to be present without logwood. Copper and iron may be used in either tannin or logwood inks. Sulphuric acid should be determined by igniting the dried residue of the ink with addition of a little sodium carbonate, and subsequent solution of the residue in hydrochloric acid and precipitation with barium chloride. Its proportion to the bases present should be calculated, as organic salts of iron are less likely to injure the leather than ferrous or ferric sulphates. Thickening matters likely to be present are sugar, gums and dextrine, and occasionally fatty substances. American blacks often contain tragacanth, which may be recognised by its large round starch cells, which only colour slowly with iodine unless the solution is very strong, probably on account of a protective covering of mucilage. Gums and dextrine may be precipitated by addition of considerable quantities of strong alcohol, while the sugars will remain in solution, and may be recognised by their reaction with Fehling's solution (p. 267).

Another class of blackings are those used on boots, in which the black consists mainly of carbon, produced by the carbonisation of some form of sugar with sulphuric acid. Bone black is frequently added to the mixture to neutralise the excess of acid, and hence calcium sulphate, phosphate, and carbonate may be found on analysis. Sugar is usually present, with some quantity of oil or fat. Pastes for coloured boots contain waxes and oils, with soaps or turpentine and aniline browns or yellows. "Quick-blacks," for shoe manufacturers are alkaline solutions of shellac and other resins or waxes with logwood or aniline blacks.

The blacks used on waxed leathers consist of lampblack with oil or soap; while in the sizes, glue, tallow, flour, gum-tragacanth and soaps are frequent constituents. Carbon blacks are

perfectly insoluble in acids or alkalis and are only destroyed by heat and powerful oxidisers. They may, therefore, always be removed by filtration after bringing the other constituents into solution by digestion with acids, alkalis and hydrolysing agents. The insoluble matter may then be collected on a tared filter and weighed, and the insoluble inorganic constituents estimated by ignition. The estimation of fats and fatty acids is frequently difficult from the presence of mucilages which cause emulsification. These may generally be hydrolysed by prolonged digestion with weak acids, or sometimes by short treatment with strong sulphuric acid, and the fats may then be removed by shaking out with petroleum ether or some other suitable solvent. It must not be forgotten that unsaturated fats are acted upon by strong sulphuric acid (p. 299). Unsaponified fats or fatty acids may often be recognised as highly refracting globules under the microscope. No general methods for the analysis of such mixtures can be given, and their investigation will usually test the ingenuity and resources of the chemist, while experience of the substances likely to be met with will be found to play an important part.

Much additional information on the analysis and detection of colouring matters will be found in Allen's 'Commercial Organic Analysis,' already quoted. In the case of mordant colours, useful hints may often be obtained by the examination of the ash for metallic bases (pp. 363-366).

Where the object of the chemist is simply to determine the dyeing value of some colour, the nature of which is known, in some cases recourse to chemical analysis may be had, though actual dye-trials will usually prove most satisfactory. Colours are often "diluted" with dextrine, sugar, salt and other indifferent matters, or salt may occur as an impurity of manufacture, being frequently used to precipitate dyes from their solutions. When colours are really identical, their relative strength may be determined by the colorimeter, or more simply by matching a dilute solution of the dye to be tested by adding a solution of a standard dye of known purity from a burette to a similar volume of water in a Nessler tube on a white surface. When the colours are equal, each tube contains the same weight of actual dye, from which the relative strengths can be calculated. If, however, the dyes are not really identical in character, such

tests are often deceptive. The tint of a dye may be matched and registered by the tintometer. (See p. 239.)

The most convenient material for dye-tests on leather is generally sumach-tanned skiver, though any other material may be used which it is intended to dye. The method of testing adopted should as far as possible be arranged on the same lines as the method actually to be adopted in dyeing. Those practically in use are "staining," in which the colour is applied to the surface with a sponge or brush; dyeing in trays, in which the goods are moved by hand; and dyeing in paddles or drums. Staining is not merely a question of painting with a coloured liquid, but it is necessary that the dye should have an affinity for the fibre. As the goods are not washed after staining, the use of sulphuric acid in any form in the staining liquor is quite inadmissible, and it is usually preferable to employ basic dyes, which not only have a great affinity for the leather, and great covering power, but can be applied without acid. If "acid" dyes are used, it is generally necessary to employ some acid to combine with the base and set free the colour-acid, and for this purpose formic acid is most suitable. Solutions of aniline colours of about 1-2 grm. per liter according to the strength and solubility of the dye are usually employed, and two or more coatings are given. The leather should be dampened before the application of the dye, and the coating should not be repeated until the leather is dry on the surface. Samples are conveniently stained on a sheet of glass. Alumed kid and chrome leather are often dyed on the table by a process very similar to staining, but mordant-colours such as the dye-woods are very frequently used. The table is generally of lead, and slightly higher in the middle, so that the surplus dye runs off to a channel round the edges. The skins are placed on the table quite wet, and spread with a sleeker, and the necessary mordants and dyes are applied with brushes, washing the skin with water between the applications to remove loose dye which might be precipitated. Dyeing in the tray is done in two different methods. The usual old-fashioned English method employs a tray usually sufficient to hold from 2-3 dozen skins, and in order to economise dye and avoid dyeing the flesh side of the skins, they are frequently "paired" flesh to flesh, or "pleated" by doubling down the back, and pressing the surfaces together on the table with a sleeker.

By careful handling, these surfaces may be maintained in contact throughout the dyeing process. Comparatively weak dye-baths are used, and acid colours are generally preferred, though basic may also be employed; and the skins are turned in the bath, often for three-quarters of an hour or more, till the bath is as completely exhausted as possible, the colour being usually added in two or three portions so as to begin in a weak bath. In the usual Continental method of dyeing, two small trays only are used, each of them capable of holding a single skin or pair of skins which are paired or pleated. The bath usually holds about 6 liters of water for small skins, and basic dyes are preferred from their rapidity of action. The dye is usually kept in a concentrated solution and diluted with hot water to the required volume, a temperature of 40° – 45° C. being suitable. The skins are dyed singly or in pairs, and each is entered in a nearly exhausted bath, and finished in a fresh concentrated one in which it is turned till dyed to shade; the dyeing usually occupying only a few minutes. An undyed skin is entered in the second bath, through which two have already been passed, and after two or three minutes' turning goes into that from which the previous skin has just been dyed out. The exhausted bath is now emptied, and a fresh one prepared in which the skin is finished, the second bath now becoming the weakest, in which a fresh skin or pair of skins is entered. Thus, though only two trays are used, each skin passes through three successive baths, and the dye liquor is fairly exhausted. In paddle and drum dyeing the proceeding is much the same as that in the old English method of tray dyeing, but in the paddle a larger volume of liquor has to be used, and in both cases the flesh as well as the grain side of the skin is dyed, thus involving a larger expenditure of colour, though effecting a considerable saving in labour. Paddles are usually sufficiently large to dye several dozen skins, and the colour is added in successive portions, the exhausted dye-bath being usually run away.

For experimental dyeing, basins of about 500 c.c. capacity, broad and shallow beakers, or porcelain or enamelled photographic trays are conveniently employed, and must be maintained at a temperature of 40° – 45° C. by placing them in a water-bath. Paddle and drum experiments are conveniently made in the churn described for colour tests on p. 240, a larger volume of

liquor being employed when it is desired to imitate the action of the paddle, and the jars being if necessary wrapped in flannel or felt to retain the heat. With acid dyes, if sulphuric acid is used, a quantity equal to half the weight of the dye is invariably sufficient. In dyeing in the basins or trays, goods must be continuously turned over, either with the fingers or with a glass rod, or after the manner of the Japanese student, with two glass rods between the fingers like chopsticks. When the dyeing is completed the pieces are taken out, rinsed with water, and squeezed and smoothed out with a brass or glass squeegee on a glass plate, and are nailed or pinned out on a board to dry. By comparing a set of samples dyed in this way it is easy to judge of the relative strength and tint of the colours, and a further idea may sometimes be obtained by dyeing a number of pieces successively, allowing longer time as the bath gets weaker. If the colour is a mixture of two or more dyes, of which the attraction for the leather is not exactly equal, the tint of the later pieces will vary from that of the earlier ones, although the depth of colour may be equal. The colour of dyed leather is made darker and fuller by finishing; and the effect of this may to some extent be judged by burnishing lines on the very slightly damaged leather with a smooth piece of wood, or the handle of a knife or toothbrush, or a sample may be glazed and finished if the appliances are at hand. The dry samples are invariably paler and duller in tone than when wet, but this is considerably recovered in the finishing process. If the dye has been allowed to precipitate in the bath, portions of it will adhere to the surface as a powder which will rub off, and if its attraction has been too great and the dyeing too rapid, it will frequently occur that when sleeked out the leather "gapes," as the dyer calls it, showing undyed portions in the less exposed minute creases of the grain. Colours which are not quite exact to shade are usually corrected by the finisher, who mixes dyes with his seasonings.

In calculating from dye-tests, 1 grm. per sq. meter is equivalent to 30.5 grm., or slightly over 1 oz. per 100 sq. feet, and 1 grm. per liter to 1 oz. per cubic foot of dye-liquor, or 1 lb. per 100 gallons.

SECTION XXIV.

THE USE OF THE MICROSCOPE.

AMONG the means of investigation at the disposal of the leather chemist, the microscope takes a most important place. It is only by its use that the minute structure of the skin can be studied, and it is constantly requisite for the examination of surface defects, such as "weak" grain and other forms of bacterial damage. It has also become very important as a means of recognising adulteration in tanning materials, and especially in sumachs. It is essential in the study of bacteriology and fermentations, which play so important a part in leather manufacture. While for many of the purposes named comparatively low powers are sufficient, for bacteriology the highest powers and the greatest accuracy of adjustment both of focus and lighting are essential. For preliminary examination of leather and many other things, a good achromatic pocket-lens of the Coddington type, and of $\frac{1}{4}$ -in. to $\frac{1}{2}$ -in. focus is almost essential, and often forms an effective substitute for the lower powers of the microscope.

While it is possible to do very useful work with a somewhat inferior instrument, it is advisable in purchasing a stand to secure that in really essential points it is of the best, although sometimes refinements such as the mechanical stage may be dispensed with. Good instruments of comparatively moderate price can now be obtained both of English and Continental opticians, but 15-20% may be put down as about the cost of a really efficient microscope to cover all the uses mentioned. Out of this, however, 5% at least will be required for an oil immersion objective for higher bacteriological work, which can generally be dispensed with at first unless bacteriology is made a speciality. If more cannot be afforded, it is better at least to obtain a solid and simple stand with a suitable sub-stage fitting for an Abbe condenser, a substantial stage, and say 1-inch and $\frac{3}{4}$ -inch objectives.

As high powers are often required in the examination both of hide sections and of ferments, which are the principal objects of investigation in a tannery, it is of the first importance that

the fine adjustment should be perfectly steady, without vibration or backlash. This is seldom or never the case with cheap microscopes, in which the fine adjustment is made by a screw at the side of the tube moving the nose by means of a lever. A much more satisfactory arrangement is that in which the whole body of the microscope is raised or lowered by a screw in a pillar at the back of the stand on which it slides. A rack for coarse adjustment is very useful but not absolutely essential. If a sliding tube only is provided, it must be tight enough not to slip, but must move easily up and down with a sort of screwing movement. A mechanical stage is not necessary, though often convenient, but for many purposes one of black glass or ebonite will fill all requirements. If a simple rotating disc with holes of various sizes is used for regulating the light, it should be as nearly level with the surface of the stage as possible, and when examined with a low power should appear in the centre of the field; but an Abbe illuminator or some similar condenser with iris diaphragm is much more convenient, and, for work on the minutest ferments, is essential. This can be fitted into the tube below the stage of the cheaper microscopes, but is much better on a separate substage with focusing and centring adjustments.

A frequent defect in cheap microscopes is that the mirror for substage illumination does not bring the rays of the lamp to a focus exactly on the object, but frequently some inches above it. This may be to a great extent overcome by the use of a bull's-eye condenser between the lamp and the microscope. Another defect is that sometimes the centre of the mirror is not in a line with that of the microscope body.

It is wise, in purchasing a microscope, to select first a good and substantial stand, to which additional fittings and objectives can be added as required. Most good stands are now fitted with the standard screw of the Royal Microscopical Society.*

The optical part of the compound microscope consists of the "objective," which is a compound lens screwing into the lower end of the microscope tube, within which it forms an enlarged

* Among English opticians, Swift and Watson may be remarked as producing very suitable microscopes of moderate price, while on the Continent, Zeiss, Reichert, and Leitz have a well deserved reputation. Figs. 23 and 24 represent good English and Continental types, which now differ but little.

image of the object, which is still further magnified by the "eyepiece," a second combination of two lenses which slides into the top of the tube. Of these, the objective is by far the more expensive and important, for no amount of magnification by the eyepiece will make anything visible which is not clearly defined in the image which the objective projects. It is also found that the "resolving power," or capability of rendering minute details, depends not merely on the magnifying power of the microscope, but on the "angular aperture" of the objective, or width of the cone of rays which it collects. The magnifying power of the objective depends simply on its focal length, with which it varies inversely. Thus objectives are known by their focal length: a "1-inch" with "A" eyepiece magnifying about 50 times, a $\frac{1}{8}$ -inch 300 times, and a $\frac{1}{12}$ about 600 times. With the "C" eyepiece the magnifications are about double those with the "A." The Continental opticians number instead of lettering their eyepieces, and their magnifying powers neither agree with the English nor with each other. It would be much better if the eyepieces as well as the objectives were described by their "equivalent focal length," that is, the focal length of a single lens of the same magnifying power. Described in this way an "A" eyepiece should be of 2 inches or 50 mm., and a "C" of 1 inch or 25 mm. equivalent focus. The magnifications given are those with a 10-inch tube. Continental, and many English microscopes are now made with a 6-inch tube, and therefore magnify less. They are mostly fitted with a "drawtube," by pulling out which the tube can be lengthened and the magnification increased. This is often very useful, but it must be remembered that an objective performs best with the length of tube for which it is adjusted; and that a lower power, if of larger aperture or greater optical perfection, will often show more than a much higher power if of inferior quality.

It must not be supposed that an objective focuses at a distance from the object equal to its nominal focal length. This is measured from the "optical centre" of the combination, and in all high-power lenses the front lens is brought as close to the object as is practicable, in order to collect the largest possible cone of rays, and thus increase both the light and the resolving power. Frequently the "working distance" is so short as to necessitate the use of the thinnest possible cover-glasses, and

the most careful focusing to avoid damage either to the object or the objective. All objects which are examined under high powers must be covered with glass, and the objectives are con-

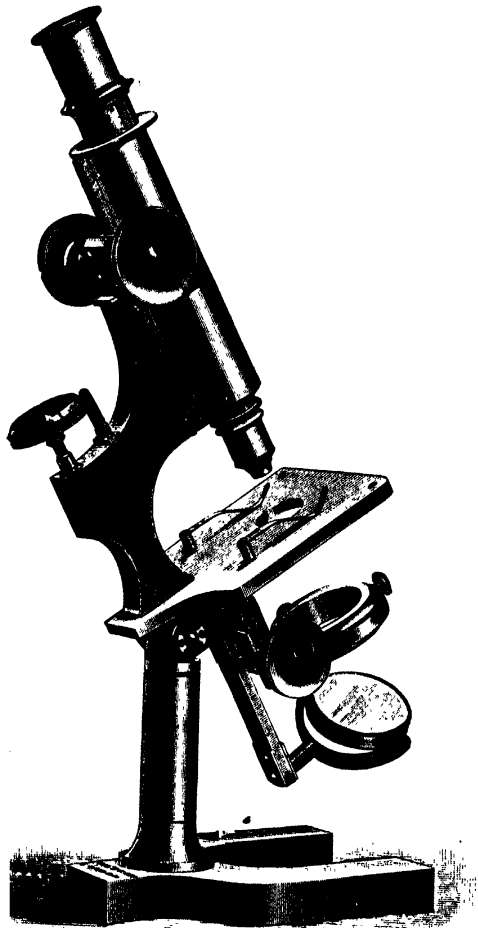


FIG. 23.

structed in view of this, the presence of the glass involving a correction which varies with its thickness. Some objectives are

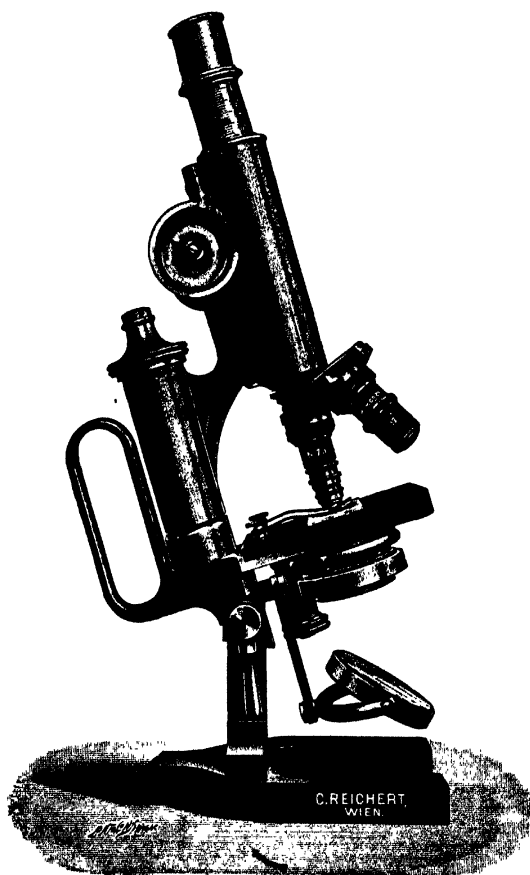


FIG. 24.

provided with a collar which varies this correction, but most are now made for use with a cover-glass of one thickness, generally

the thinnest to be had, and this is the most convenient arrangement. Where a variable correction is provided, it is used by focusing on some test-object, such as a diatom, and then altering the correction collar, at the same time keeping the focus right with the fine adjustment till the best definition is obtained. This is very troublesome, and is best made once for all. Slight variations of thickness of cover-glass may be corrected by the drawtube—the thicker the glass, the shorter the tube required.

The objectives which have so far been described are “dry,” that is, a space of air exists between the cover-glass and the front lens. By a well-known law of optics, a ray cannot pass out of water or glass into air, at more than a certain angle with the surface, but is “totally reflected” back. This effect may be seen by looking upwards at the surface of water through the side of a tumbler, when it will be found impossible to see through it if the angle exceeds a certain amount. For glass this is about 41° , and hence it is impossible to obtain from an object in balsam under glass, a cone of rays of which the sides are inclined to each other at an angle of more than 82° , all rays beyond this being reflected downwards. If, however, a drop of water be interposed between the glass and the front surface of the objective, this effect is greatly diminished, and if for water a liquid be substituted such as cedar oil, which has practically the same refractive power as glass, it disappears entirely, and all the rays can reach the objective which it is capable of collecting. Objectives constructed to be used in this way are known as “immersion objectives,” and those using oil of equal refractive index to the glass are styled “oil” or “homogeneous” immersions. Either oil- or water-immersions can be made of wider angle than corresponds to an air-angle of 180° , and the oil-immersion $\frac{1}{2}$ has proved almost indispensable in bacteriological studies.

The most useful objectives for the leather manufacturer are the 1-inch and $\frac{1}{2}$ -inch dry, to which may be added the $\frac{1}{2}$ oil-immersion for bacteriological work. The latter is only essential for actual study of bacteria, as most ordinary forms can be seen, and in many cases their species distinguished, by a good $\frac{1}{2}$ of wide angle. Where the $\frac{1}{2}$ is also provided, a $\frac{1}{6}$ of some-

what smaller angle will suffice, and will be found cheaper and more convenient in use on account of its greater working distance.

Illumination is one of the most important points in practical microscopy. With powers of not less than half-inch focus, objects may generally be examined by light thrown upon them from above by a bull's-eye condenser, or by good daylight. In this case they need not be transparent or specially prepared; and the plan is often convenient for a mere surface examination. In examining bodies illuminated in this way, prominences frequently appear as hollows and *vice versa*, by a sort of optical illusion, which, once established, is very difficult to overcome. By remembering the direction of the light, and that this appears reversed in the microscope, it is easy to decide the truth.

For all finer work and higher powers, and most generally with the low powers also, it is necessary to render the object transparent, and to examine it by light transmitted from the mirror below the stage.

Good daylight is least trying to the eyes. Where artificial light must be used, that of a small paraffin, incandescent gas, or electric lamp is best; and a blue chimney, or blue glass interposed between the stage and mirror, or lamp and microscope, spares the sight, and makes it easier to distinguish colours. The light should be sufficient, but not too dazzling. Work should never be prolonged after the least strain is felt, nor should the microscope be used for some little time after a meal. It is well to accustom oneself to keep both eyes open while observing.

In observing in daylight it is usually best to use the plane side of the mirror, but with the lamp, the concave side must be employed and its distance from the lamp and below the stage so chosen that the light is brought to a focus on the object. If, as is sometimes the case, the focus of the mirror is too long to allow of this, it may be shortened by interposing the bull's-eye condenser between the lamp and the microscope, or by a condensing lens fitted below the stage. In most cases the centre of the mirror should be in the line of the centre of the tube, but some objects, and especially diatoms, are best seen by oblique

light. The use of various apertures of the revolving diaphragm will assist in the making out of structure, the smaller apertures practically narrowing the angle of the lens, and increasing its penetration (the power of distinguishing objects slightly out of focus) while at the same time the resolving power is somewhat diminished.

If the microscope is furnished with the Abbe illuminator with iris diaphragm, all other means of using transmitted light will be found to be more or less makeshifts, accomplishing with difficulty what it will do with ease, and with much greater perfection; and, especially, the power given by the iris of varying the illumination gradually from bright to dark, or wide to narrow angle is most useful, though it is only with high powers, and particularly for bacteriological work that it is indispensable. With the Abbe illuminator or any other substage condenser, the plane side of the mirror should be used.

Focusing.—It will be obvious from what has been said, that with the higher powers the greatest care is needed to avoid screwing the objective down on the cover, and so breaking one or both of them. One way to avoid this is to screw down as close as possible to begin with, and then focus upwards. Another plan, when the object on the slide is small, is to keep continuously moving the slide gently with the fingers while looking into the tube. It is then easy to notice when the dust and small particles on the slide come into focus, and if the point should happen to be overstepped the contact will generally be felt before serious damage is done.

While observing, the fingers should be kept on the focusing adjustment, which should be continuously slightly varied, so as to look into the object in its various planes of depth, and to learn their relations. In this way many points of structure become clear, which could not have been distinguished while only one plane was visible. It must always be remembered that with high-powered and wide-angled objectives only a very thin plane can be seen at once, to which the thinnest section which can be cut has a relatively great depth, so that the picture may be very different as we focus on the upper or the lower layers. A curious point which may be noticed is, that under these circumstances we can apparently see through opaque objects if they are of small size. A hair, for instance, on the upper surface may become

quite invisible if we focus on something below it, of which a perfect image is formed by the outer rays of the cone of light, which pass round its sides.

By varying the focus we can distinguish between air-bubbles and oil-globules, both of which will be early encountered by the microscopist, and are so far puzzling to the beginner that, in a well-known Continental work on tanning the former are clearly described and figured as a new form of albumen! Both form regular circular objects, which, in certain positions of the focus are surrounded with a clear dark outline. On screwing the objective downwards this broadens, and the centre brightens in the case of the air-bubble, while in the oil-globules the edge becomes lighter and the dark ring moves inwards, and becomes hazy and indistinct and the centre shaded. When the objective is raised the reverse changes take place in the two objects. When both oil, and air-globules are present, it will be noted that the dark margins of the former are much narrower than those of the latter, and that oil-globules often act as small lenses, in which images of outside objects, such as the window bars may be distinguished. Oil- and fat-globules may be observed in most glues and gelatines when dissolved or swollen in water, and are one of the principal causes of their opacity. Their size and number is often worth observing in fat liquors, egg substitutes, and suchlike preparations, as an index of the quantity of oil present, and the perfection of the emulsification.

Preparation and Mounting of Objects.—Very few objects can be examined under the microscope without some sort of preparation. To study the grain of leather under low powers, a small piece may be laid on a glass slip, with its surface as level as possible, and examined under a 1-inch objective by reflected light of which the direction should be varied by moving either the light or the object, so as to see it under as many aspects as possible. In the same way a thin slice showing the cut or section of the leather may be examined, when the fibre bundles and their finer and closer arrangement in the grain layer, the dark glossy ends of the cut bundles, and sometimes crystals and concretions of catechin (the "whites"), of glucose or barytes, and other weighting material may be detected. In a similar way ground tanning materials may often be examined with advantage, a small quantity being dusted on a slip, and compared with a

sample of known quality, when adulteration with other vegetable matters or with sand may be detected.*

All objects which are to be examined with high powers require the use of transmitted light. The easiest to deal with are those which are sufficiently small or soft to form a thin layer under a cover-glass without being cut into sections. Generally such objects are examined, in water or glycerine, but if naturally transparent, the dry state is sometimes advantageous, e.g. starches and crystals. Take a little arrowroot or potato starch, and dust so small a quantity on a glass slip as to leave a little whitish cloud; place it on the stage of the microscope, which should be horizontal, and cover with a thin glass. It may now be examined by transmitted light under the $\frac{1}{4}$ or $\frac{1}{8}$ objective. The starch granules will be seen as flattened ovals. By careful focusing and lighting, the little spot known as the *hilum* will be seen near one end, while the surface of the granule is marked with rings, of which the *hilum* is the centre. Most other starches are smaller than those named, and frequently different in form. While potato starch may reach a length of $180\ \mu$ (thousandths of a millimeter), rice starch forms small polygonal grains, which do not exceed $6\ \mu$ in length. Many starches and especially those of the bean tribe, have radiating cracks round the *hilum*. A good plate showing the forms of the most important starches may be found in Allen's 'Commercial Analysis,' vol. i. Starches are very widely distributed in the vegetable kingdom, in fruits, roots, and even the barks of trees. Those of some of the tanning materials are very characteristic (e.g. Angica bark, canaigre, etc.). Useful hints may often be obtained by detection and identification of starch grains, as to the farinaceous materials used in the tawing and finishing of leather. Such observations are best confirmed by direct comparison with genuine samples of the starches suspected.

So far I have spoken only of the dry examination of the starch. Let it now be mixed with a little water and a cover-glass gently laid on with forceps, so as to avoid the formation of bubbles. It will probably be found more difficult to see the rounded form of the granules, and if glycerine be substituted for

* For many of these purposes, the pocket-lens may be advantageously employed; its portability and greater depth of focus doing much to compensate for its inferior magnifying power.

water, this will be still more so, while the granules will appear flat and almost entirely transparent. This illustrates a general principle in microscopy, to the cause of which attention must be drawn. If a glass rod be looked at in air, its form will be clear, and any markings on its surface distinctly visible. Let it now be plunged successively in water, glycerine, clove oil or turpentine, and bisulphide of carbon. It will become less and less visible until, in the last, it will almost disappear. If the experiment be repeated with a tuft of glass wool, or with glass powder, it will be found quite white and opaque in the air, while in the carbon bisulphide it will be transparent, so that print can be read distinctly through it. A little consideration will make the cause of this clear. The glass in itself is perfectly transparent, but at its surface the light is refracted and reflected in all directions, instead of passing into and through it. If it is brought into a liquid which has practically the same index of refraction as glass, it becomes for optical purposes like a solid block, through which the light passes without interference. The minute structures which are observed under the microscope may mostly be regarded as transparent, and when brought into media which, like glycerine, clove oil and balsam, are of nearly the same refractive power as themselves, they are cleared up in the same way as the glass powder. This is often extremely useful in enabling us to see into structures under the microscope, but, as we have seen, it renders their outside form less visible. To get over this difficulty we resort to processes of staining, which make the structure visible by differences of colour.

Place a small drop of a solution of iodine in iodide of potassium in contact with one side of the cover-glass which is over the starch, and at the opposite side lay a little slip of blotting paper, and watch the result under the microscope. The iodine solution will be drawn under the glass, and will stain the starch granules deep indigo blue. This is a most useful method of recognising starch. Many of the coal-tar colours dissolved in water or alcohol are useful stains for vegetable matters, and bacteria, while for animal sections polychromatic colours such as carmine and logwood are more generally useful, as their dyeing is more selective, and enables different kinds of tissue to be more readily distinguished.

If the microscope is provided with polarising apparatus the

starch granules observed with crossed Nicol prisms appear light on a dark ground, with a characteristic bright cross, which changes from light to dark on rotating the analyser. The polariscope is a very useful addition to the chemist's microscope, but for details books on microscopy must be consulted.

Fibres, powders and pasty materials of various kinds may be

examined in water, like the starch, and may be stained in various ways if necessary. For many materials a useful and easy mode of preparation consists in teasing with a pair of needles, or even rubbing up in a mortar. Such needles are sold by opticians, or may be made by taking a common sewing needle, breaking off short with a pair of pliers, forcing the point into the end of a piece of wooden penholder to make a hole, and then pushing in the broken end with the pliers. A minute fragment of hide or leather may be teased in this way in a drop of water or glycerine, on a glass slip, and the fibres, if desired, stained with logwood or an aniline colour (see p. 423), when they may be examined under the highest powers. Com-

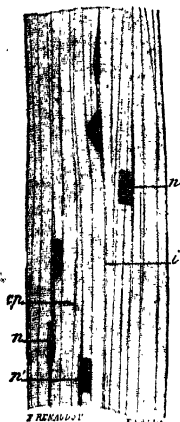


FIG. 25.—Muscular Fibre.

parison of hide fibres treated with different depilatories or tanning processes is both interesting and useful. A shred of lean meat, preferably cooked, will be found an interesting object for comparison, the muscle-bundles being somewhat similar to those of the hide; but the finest fibres will show under the $\frac{1}{2}$ objective the cross-stripping which is characteristic of all voluntary muscles.

In order to get a clear idea of general structure, it is in almost all cases necessary to make sections. Vegetable sections are easier to cut than animal, and a raw potato, carrot or radish is a good object to practise on. The potato will cut better if first cut into pieces of perhaps a quarter of an inch square, and hardened by soaking first in dilute and then in strong methylated spirit for a day or two, which withdraws the superfluous water. The strip is now taken between the finger and thumb, as shown in Fig. 26, and with a sharp razor, flooded with dilute

THE USE OF THE MICROSCOPE.

alcohol, and resting on the tip of the forefinger, a thin shaving is taken off the top of the strip, using either a drawing or pushing cut, as may be found most convenient to the individual worker.

The section, when cut, is removed carefully by a camel's-hair brush dipped in dilute spirits, rather by floating than pushing, and is placed in a watch-glass or small porcelain basin in spirits or water. Sometimes water may be substituted for alcohol in cutting, but the latter is more generally useful. It will be found at first that few of the

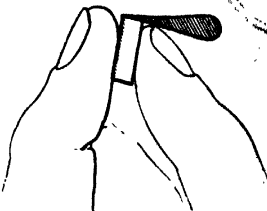


FIG. 26.

sections are thin enough, and it is best to cut a good number and, rejecting the thicker, select the thinnest only for use. These may now be examined in water under a cover-glass, and, if necessary, stained with iodine solution, which will colour the starch blue, as before, and the protoplasm of the cells yellow. A thin section, even if torn, is often more useful than a perfect one of greater thickness.

Pieces of liver or kidney, hardened in alcohol, are also very good objects for practice, and if desired may be stained and permanently mounted like hide sections (see p. 423). Small or thin pieces are conveniently held between pieces of cork, elder pith, or even slices of carrot, or embedded in paraffin wax or a mixture of stearine and naphthaline, by filling a little square mould of paper with the melted mixture, and then, as it begins to set, but not before, holding the piece of tissue in it with a needle or forceps till it solidifies. The block may afterwards be trimmed into convenient form for cutting.

It will be found impossible by freehand cutting to get large, even sections like those of the shops, which are cut with the microtome, but some part will probably be found thin enough for examination, and it is almost impossible to cut sections of skin exactly in the right direction with the microtome, though it is very useful for tanning materials, etc. Descriptions of the modes of using it will be found in books on practical microscopy, to which the reader is referred. The Cathcart microtome is a good and cheap form, which is available both for freezing and embedding.

Apart from the study of structure, the microscope will be found useful in the identification of minute quantities of substance by chemical reactions. Crystals may be recognised by their form, and, where polarising apparatus is available, by their action on polarised light, which often gives rise to gorgeous chromatic effects. Under a low power, minute portions of chemical reagents may be added, either on an open slip, or, like the iodine

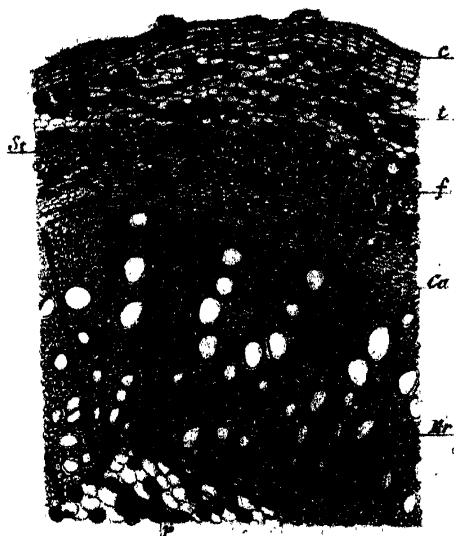


FIG. 27.—Section of oak twig stained with ferric salt, showing distribution of tannin (Bastin); *c*. corky layer; *t*. tannin cells; *St*. stone-cells; *Ca*. cambium; *Mr*. medullary ray; *p*. pith.

solution with starch, under a cover-glass. Iron may, for instance be recognised by its action with tannin or ferrocyanides, carbonates by the production of gas-bubbles in presence of acids (best seen under a cover-glass), tannin in plant cells, etc., by its reaction with iron, fat by blackening with osmic acid, and so on.

Further details of microscopic work will be given in connection with the special cases in which it is applied, but much

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additional information on staining and preparation will be found in Lee's* 'Microtometist's Vade-mecum,' Zimmermann's† 'Microtechnique,' and works on special branches such as botany, bacteriology, and histology.

It is important that the student should be provided with means of measuring and of drawing to scale the objects which he observes with the microscope. One of the simplest appliances for the purpose is a small disc of glass, ruled in squares, which is slipped into the eyepiece of the microscope. By using the ordinary square-ruled paper employed by engineers for sectional drawings, any one with a little experience in freehand drawing can make an accurate representation of what he sees, at least as regards outlines, and if a stage micrometer (a glass slide ruled in hundredths of a millimeter or thousandths of an inch) be substituted for the object, it also can be sketched in, and will then form a scale by which the size of the object can be directly measured on the sketch. If the microscope is provided, as it should be, with a graduated draw-tube by which the magnification can be varied, it is easy to bring the image given by any objective and eyepiece to such a size that some even number of divisions of the stage-micrometer coincide with one square of the eyepiece glass; and if this is noted once for all, and the sketch is made with the same length of draw-tube, no further measurement is required. Some microscopes have an eyepiece scale instead of a square ruling, and this can be used in the same way for measuring, but is not convenient for drawing.

Drawings may also be made by the camera lucida, which consists either of a prism or transparent mirror, fitting on the eyepiece in such a way that, by placing the microscope horizontally on a box or other stand, so as to raise it about 10 inches above the table, and looking down through the camera at right angles to the body of the microscope, the reflected image of the object can be seen at the same time as a sheet of paper laid or fastened on the table on which it can be drawn. Instruments are also constructed in which the horizontal position of the microscope is unnecessary. The focus of the microscope must

* Lee (A. B.) 'The Microtometist's Vade-mecum.' Handbook of Methods of Microscopic Anatomy. Sixth Edition, 1905. (Churchill.)

† Zimmermann (A.) 'Botanical Microtechnique.' A Handbook of Methods for the Preparation, etc., and Microscopical Investigation of Vegetable Structures. Translated by J. E. Humphrey, 1896. (Archibald Constable and Co.).

be so adjusted that lines on the paper can be seen clearly at the same time as the object, and that slight movement of the eye causes no movement of the one over the other. The light must also be so regulated by the iris or otherwise that both can be seen at once, which is not always easy. By using square-ruled paper, it is obvious that objects can be drawn to scale and measured as before described. A simple camera lucida may be improvised from a thin cover-glass fixed at an angle of 45° with the eyepiece, with cork and cardboard.

The dimensions of microscopic objects are now generally given in μ , or thousandths of a millimeter; 0.001 of an inch is approximately 0.025 millimeters, or 25 μ .

Drawing is now to a considerable extent superseded by photographic methods, which are not only more accurate, but effect a great saving of time where many representations are required, and involve no very costly apparatus, nor special skill, unless very high powers are employed. Very good work has been done with an ordinary $\frac{1}{4}$ -plate camera lengthened with an improvised cardboard tube. It is desirable that both microscope and camera should be screwed or clamped on to a single base-board, which may also carry the illuminating lamp, for which an incandescent burner for gas, or a Nernst projection lamp for electricity is well adapted. It is almost essential if a long camera is used to devise some means of adjusting the focus from the screen end, either by moving the latter, or by mechanically operating the focusing screw, which in some microscopes has a groove round which an india-rubber band can be placed to act as a belt. It is also very convenient to be able to adjust the position of an object by a mechanical stage operated from the screen.

Powers of moderate angle are usually most convenient for ordinary work, and where any "depth of focus" is needed, a somewhat low power and a long camera gives the best results. Unless a special projection eyepiece is available, it is usually best to use the objective only, which then takes the place of the ordinary camera lens. Different objectives of equal quality for ordinary work sometimes differ widely in their photographic properties, and as they are not specially achromatised for ultra-violet rays, some correction of focus is often required, usually in the direction of shortened focus. If a photograph shows less definition than the visual image, a first approximation may be

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made by throwing the visual image out of focus to approximately the same degree of indistinctness; and the correction, once found, can be noted for future use. The employment of isochromatic (and backed) plates tend to lessen the chromatic error. Colour screens may also be used.

One of the most important applications of microscopic examination for the tanner is in the detection of adulteration in sumachs and other finely ground tanning materials. In the case of sumach especially, adulteration has been in the past rather the rule than the exception, and as some of the adulterants are not only inferior in tanning strength, but contain catechol tannins which redden on exposure to light, their detection is of considerable importance.

In the case of leaf sumach, it would not be difficult to pick out the fragments of *rhus coriaria* by direct examination under a low power with reflected light, as the hairs on the leaf are very characteristic, but in the fine powder this is impossible, while it is too opaque for examination with higher powers and transmitted light. The first and perhaps the most complete work on the structure and adulterants of sumach was done by Andreasch,* when during his last illness he was obliged to winter in Sicily; and with well repaid study, but it is too detailed for useful abstraction, and has in some respects been superseded by later methods. A valuable observation was made by Lamb and Harrison† which affords the most convenient method of detecting the usual adulterants. While the internal structure of most leaves is completely destroyed by a short heating with strong nitric acid the upper and lower cuticles are much more resistant, and often have very marked and characteristic structures. The cuticle



FIG. 28.—*Rhus coriaria*.

* Sicilianische Sumach und seine Verfälschung, Wien, 1898.

† Journ. Soc. Dyers and Colorists, March 1899.

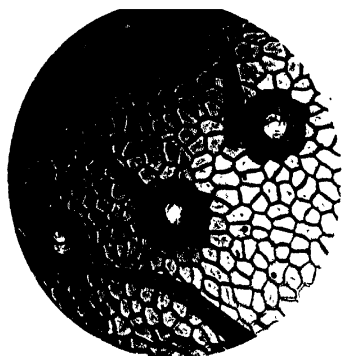
themselves vary much in resistance to the reagent, that of sumach itself being delicate and easily destroyed, while that of the common adulterant *pistacia lentiscus* (lentisque, pistacio) is extremely strong, and remains almost uninjured after the sumach is totally destroyed. Probably the best mode of procedure is that given by Priestman,* who heats the samples with strong nitric acid in test-tubes, in a water-bath containing about 750 c.c. of water, over a single Bunsen burner, beginning cold, and raising the bath to a definite temperature. After the heating is completed, the acid is neutralised with ammonia or caustic soda, and the sediment is allowed to settle, and repeated portions (7 or 8) are examined under a cover-glass. For direct examination, staining is not usually necessary, since most cuticles, and especially pistacio, are coloured distinctly yellow by the nitric acid, but for photographic purposes staining with safranin or acid red, and the use of isochromatic plates is advisable. For permanent mounting, the stained and washed cuticles may be dehydrated with alcohol, and mounted in balsam or dammar in the usual way (p. 423), though some delicate cuticles photograph better if dehydration is omitted, and glycerine jelly is used as a mountant.

The photographs on plates I., II. and III. were taken with a Zeiss B objective, which was also frequently used for direct examination. The following table summarises the effects of heating for various of the more common sumach substitutes and adulterants.

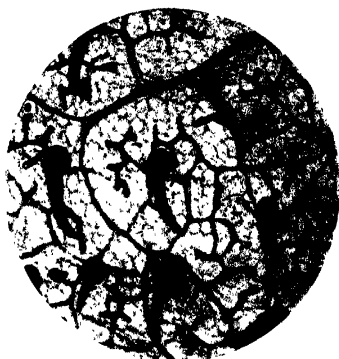
—	Cuticles separate at	Totally dissolved at
<i>Rhus coriaria</i> leaves	60-65° in 10 mins.	98° in 15 mins. from cold.
" " stems	75 " 10 "	95-98 " 15 " " "
<i>Tamarix</i> stems	80 " 10 "	90 " 15 " " "
<i>Pistacia lentiscus</i>	65 " 10 "	98 " 20 " " "
<i>Coparia myrtifolia</i>	75 " 10 "	98 " 20 " " "
<i>Rhus metopium</i>	70 " 15 "	98 " 25 " " "
<i>Rhus glabra</i>	75 " 15 "	Insol. Insol.
<i>Cotopoon compressa</i>	80 " 15 "	98° " 25 " " "
<i>Ailanthus glandulosa</i>	75 " 15 "	Insol. Insol.

Rhus coriaria. Both upper and lower cuticles separate at 70-80° C. without manipulation, but are very delicate and transparent, and the hairs, which are extremely characteristic, and quite unlike anything found in the adulterants, can hardly be seen with-

* Journ. Soc. Chem. Ind., p. 231, 1905. Collegium, pp. 184, 199, 1905.



1. *Rhus coriaria*, upper. $\times 84$.



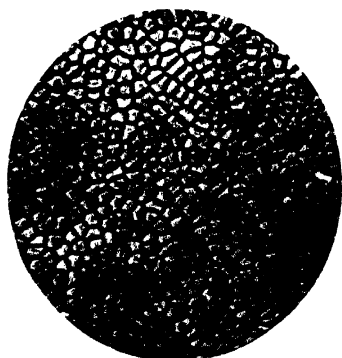
2. *Rhus coriaria*, upper. $\times 84$.



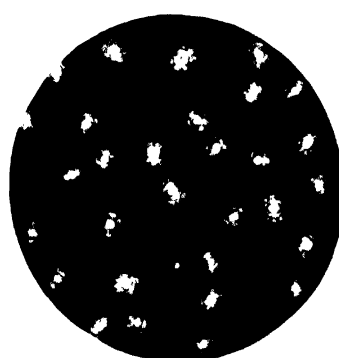
3. *Rhus coriaria*, lower. $\times 84$.



4. *Rhus coriaria*, stem cuticle. $\times 84$.



5. *Pistacia lentiscus*, upper. $\times 84$.



6. *Pistacia lentiscus*, lower. $\times 84$.



7. *Tamarix*, cuticle. $\times 84$.



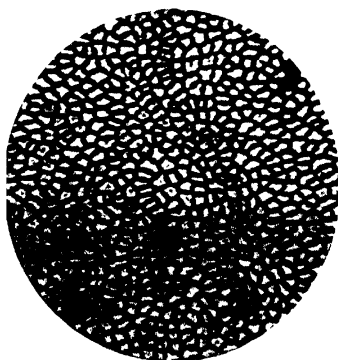
8. *Tamarix*, cuticle and fibre core. $\times 42$.



9. *Tamarix*, core fibres. $\times 84$.



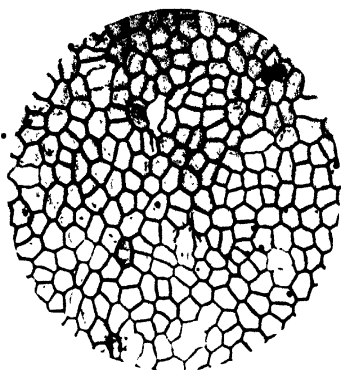
10. *Arbutus unio*, substance and cuticle. $\times 42$.



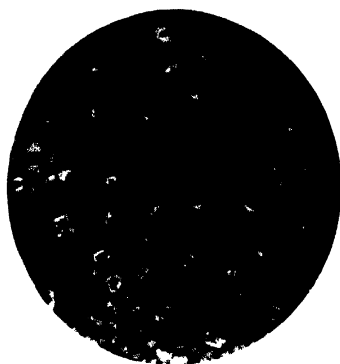
11. *Ceratonia siliqua*, upper. $\times 84$.



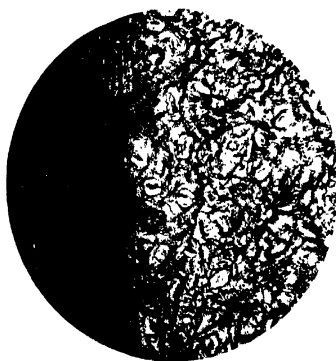
12. *Vitis vinifera*, upper. $\times 84$.



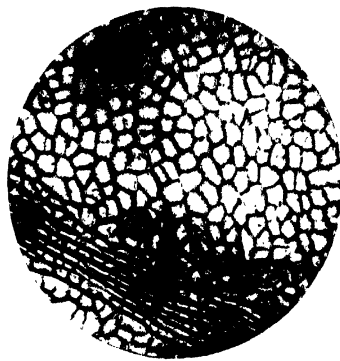
13. *Corsaria mytilifolia*, upper. $\times 84$.



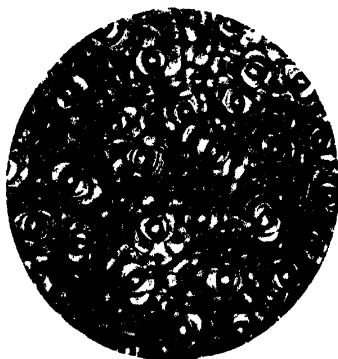
14. *Corsaria mytilifolia*, lower. $\times 84$.



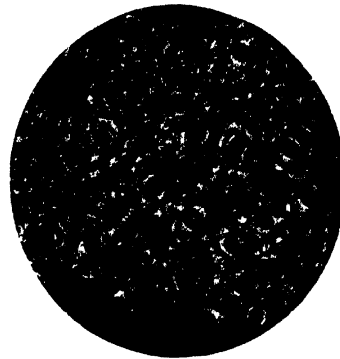
15. *Ailanthus glandulosa*, upper. $\times 84$.



16. *Ailanthus glandulosa*, upper. $\times 84$.



17. *Colpoen compressa*, upper. $\times 84$.



18. *Colpoen compressa*, lower. $\times 84$.

out staining. The hairs take the dye much more readily than the cuticles themselves. (Plate I., Figs. 1, 2, 3. Upper cuticle, Fig. 4.)

Rhus glabra, an American sumach, has small club-shaped hairs, and minute stomata on its lower cuticle, which is extremely thin and transparent, and very difficult to see or photograph. The upper cuticle is strong, and resists boiling nitric acid for a considerable time. It has a well defined cell-structure without stomata, but with frequent vein-marks. (Fig. 29.)

Rhus metopium, another American sumach, has no hairs, and strongly resembles pistacio in the form of its cells.

Pistacia lentiscus (Schinia, lentisque) was formerly the principal adulterant, but has proved so easy to detect that its use is diminishing. Its cuticles are strong, and resist acid well, their cell structure is characteristic, and they dye deep yellow with nitric acid. The reaction with nitric acid is usually more violent than with pure sumach. The cuticles separate well, and will stand the action of boiling nitric acid a few minutes longer than real sumach (Plate I., Figs. 5, 6). Only the lower cuticle has stomata, which are numerous. The cuticles are free from hairs, and but little distorted over the veins.

Coriaria myrtifolia ("stinco," redoul, French sumach) has a well defined cell-structure in both upper and lower cuticles, the cell-walls are defined, and the cuticles are easily separated by warming to 65° or 70° C. in pure nitric acid. The structure somewhat resembles pistacio, but there is a curious waviness in the well defined walls which makes it easy to distinguish. The upper cuticle has no stomata, and the cells are elongated and distorted over the veins, a further distinction from pistacio. The lower cuticle has numerous well defined stomata. (Plate III.,

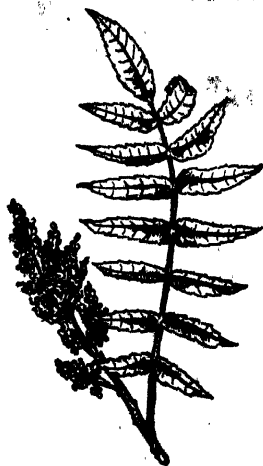


FIG. 29.—*Rhus glabra*.

Tamarix Africana (tamarisk), is a shrub with very minute leaves, so that the powder used in adulteration consists mainly of stem. The stem-cuticle has a well-defined structure of cells elongated in the direction of growth, with stomata and no hairs. The cuticle begins to separate at 70-75° C., but the woody fibre is not destroyed below 80-85° C., and as the cuticle itself is soluble a little over 90° it is well to maintain the heat for some little time below 75° rather than use a higher temperature for a shorter time. The true sumach stems behave in a very similar way, and their woody tissue much resembles that of *Tamarix*, but the cuticle of the latter is easily distinguished by the absence of hairs.

Ground Vine Leaves. The cuticles are both thin, difficult to separate from the leaf-substance, or to observe under the microscope, and their structure is not very characteristic. The vine leaf contains scarcely any tannin, but injures the colour of the sumach in tanning.

Ceratonia siliqua (carob or locust bean, caroubier). The structure of the leaf-cuticles so much resembles that of pistacio that it would probably be impossible to swear to one or the other if present in small quantities. This adulterant seems to be increasingly employed.

Arbutus unedo (arbutus, arbusier) seems less used than formerly, but in structure so closely resembles *Tamarix* that definite distinction is often impossible.

Plates of several other adulterants are given, but for further details the original papers must be consulted. It is always wiser if possible, to confirm identifications by direct comparison with known specimens, rather than trust to photographs merely. Beside microscopic examination, the chapter on the qualitative recognition of tannins by chemical tests (Sect. IX.) may be consulted, but on the whole chemical tests have not proved very reliable, and testing for catechol tannins by bromine water seems the most important. It is impossible for the chemist to recognise all the various vegetable materials which may be added to sumach; sumach stems and inferior sumachs can hardly be considered as adulterants, but may largely reduce the tanning value, and it is always possible to make use of exhausted and re-dried sumach leaves, which of course cannot be detected microscopically. If a sumach shows 28 per cent. of tanning

matter or over by the I.T.A. test, and the absence of vegetable tannins by bromine water, there is not much fear of adulteration, as few or no tanning materials of that strength are cheaper than genuine sumach.

Dr. Hellon states that the following treatment is very effective in giving a beautifully transparent residue for microscopical examination, and possesses the further advantage over the strong nitric acid process that there is no gelatinising of the vegetable matter and consequently the residues settle so rapidly from the various disintegrating liquors that the treatment may be completed without setting down the test tube out of the hand.

1. A decigram of the sample is boiled for $\frac{1}{2}$ minute with say 7 c.c. 5 per cent. H_2SO_4 , and the clear liquid poured away.

2. The residue is then boiled for $\frac{1}{2}$ minute with 7 c.c. 5 per cent. $NaHO$ solution, and the liquid poured away.

3. The residue is boiled for $\frac{1}{2}$ minute with 7 c.c. HNO_3 sp. gr. 1.2, and the clear liquid poured away.

4. The residue is boiled as before with another portion of HNO_3 , and during the boiling a centigram of $KClO_3$ is added from time to time until the substance is absolutely white. The clear liquid is poured away, and the residue washed free from acid with warm water, transferred to the microscope slide, covered and examined.

This method certainly gives beautiful preparations, though in the Author's laboratory it has not superseded that of Priestman.

SECTION XXV.

THE MICROSCOPIC STRUCTURE OF SKIN.

THOUGH a great variety of skins of the Mammalia are employed in tanning, they all possess the same general structure, and an anatomical description of that of the ox will apply almost equally to those of the sheep, goat and calf, although from varieties in thickness and closeness of texture, their practical uses differ widely. The differences between these and fish, lizard, alligator and serpent skins are much more marked.

In its natural condition, the skin is not merely a covering for the animal, but at the same time an organ of sense, and of secretion, and hence its structure is somewhat complicated. It

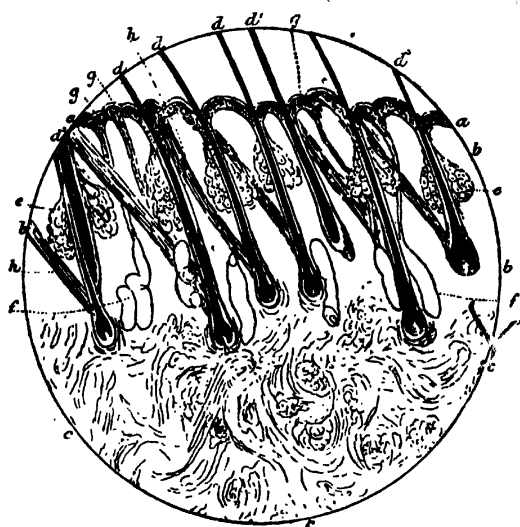


FIG. 30.—Vertical Section of Calf-skin, magnified 50 diam. : *a*, epithelial layer or *epidermis*, consisting of horny layer above, and *rete malpighi* below; *b*, *pars papillaris*, and *c*, *pars reticularis* of *corium*; *d*, hairs; *e*, sebaceous or fat-glands; *f*, sudoriferous or sweat-glands; *g*, opening of ducts of sweat-glands; *h*, *erectores pili* muscles, for erecting the hair.



FIG. 31.—Development of young Hair.

FIG. 32.—Section of Epidermis.

consists of two principal layers, the *epidermis* (*epithelium*, cuticle) and the *corium* (*derma*, *cutis*, or true skin). These are totally distinct, not only in structure and functions, but in their origin.

In the egg of birds and the *ovum* of higher animals, the living germ consists of a single cell, which, as soon as fertilised, begins to multiply by repeated division. The mass of cells thus formed early differentiates into three distinct layers, from the upper of which the epithelium arises, while the true skin, together with the bones and cartilages, is derived from the middle one.

This distinction of origin corresponds with a wide difference of both anatomical and chemical characteristics. The *epidermis* is very thin as compared with the true skin which it covers, and is entirely removed preparatory to tanning; it nevertheless possesses important functions. It is shown in Fig. 30 at *a*, and more highly magnified in Fig. 32. Its inner mucous layer *b*, the *rete malpighi*, which rests upon the true skin *c*, is soft, and composed of living nucleated cells, which multiply by division and form cell-walls of keratin. They are elongated in the deeper layers, and gradually become flattened as they approach the surface, where they dry up, and form the horny layer *a*. This last is being constantly worn away, and thrown off as dead scales of skin; and as constantly renewed from below, by the multiplication of the cells. It is from this epithelial layer that the hair, as well as the sweat- and fat-glands, are developed. It will be seen in Fig. 30 that each hair is surrounded by a sheath, which is continuous with the epidermis. In embryonic development, a small knob of cells forms on the under side of the *epidermis*, opposite to a knot of a capillary blood-vessels in the *corium*, and this enlarges and sinks deeper into the true skin, while the root of the young hair is formed within it surrounding the capillaries, from which it derives nourishment and which forms the "hair papilla"; this is shown in Fig. 31, *a b*. Smaller projections also form on the stalk of the knob, and in due time produce the sebaceous glands. The process of development of the sudoriferous glands is very similar to that of the hairs. There is a great analogy between this process and that of the ordinary renewal of hair in the adult animal. At *d*¹, Fig. 30, is seen an old and worn-out hair. It is shrunken and elongated, and is almost ready to fall out. It will be noticed that its sheath or follicle projects somewhat below the hair to the right. This is the first stage in the production of a young hair, and is quite analogous to the knob of epithelium which forms the starting-point of a hair in embryo. At *d*² the process is further advanced,

the young hair growing into the old sheath. At d^3 it is complete, the old having fallen out, and the young one taken its place.

The hair itself is covered with a layer of overlapping scales, like the slates on a roof, but of irregular form. These give it a serrated outline at the sides, strongly developed in wool and some furs, to which it gives the property of felting. Within these scales, which are called the "hair cuticle," is a fibrous substance which forms the body of the hair; and sometimes, but not



FIG. 33.
Hair Bulbs and Sudiferous Glands.



FIG. 34.
The same more highly magnified.

always, there is also a central and cellular pith, which under the microscope frequently appears black and opaque, from the optical effect of imprisoned air. On boiling or long soaking in water, alcohol or turpentine, the air-spaces become saturated with the liquid, and then appear transparent.

The fibrous part of the hair is made up of long spindle-shaped cells, and contains the pigment which gives the hair its colour. The hair of the deer differs from that of most other animals in being almost wholly formed of polygonal cells, which, in white hairs, are usually filled with air. At its base the hair swells

into a bulb, which is hollow, and rests on the hair papilla *h*, Fig. 35 (*v. s.*), which has blood-vessels and nerves, and supplies nourishment to the hair. The hair-bulb is composed of round soft cells, which multiply rapidly, and press upward through the hair-sheath becoming elongated and hardened, and forming the hair. In dark hairs, both the cells of the hair and its sheath are strongly pigmented, but the hair much the more so, and hence the bulb has usually a distinct dark form. The dark-haired portions of a hide from which the hair has been removed by liming still remain coloured, from the pigmented cells of the hair-sheaths, which can only be got out completely by bating and scudding. The cells outside the bulb, shown at *f* in Fig. 35, pass upwards as they grow, and form a distinct coating around the hair, which is called the "inner root-sheath." This again consists of two separate layers, of which the inner is "Huxley's," the outer "Henle's." They arise from the same cells in the base of the hair; but in the inner layer these remain polygonal and nucleated, while in the outer they become spindle-shaped and without nuclei. The inner root-sheath does not extend to the surface of the skin, but dies away below the sebaceous glands. Fig. 35 represents an ox-hair root, mag. 200 diam. : *a*, fibrous substance of hair; *b*, hair cuticle; *c*, inner root-sheath; *d*, outer root-sheath; *e*, dermic coat of hair-sheath; *f*, origin of inner-sheath; *g*, bulb; *h*, hair-papilla.



FIG. 35.

Outside the inner root-sheath is a layer of nucleated cells, continuous with those of the *epidermis*, and of the same character. This is the "outer root-sheath," and is shown at *d*, Fig. 35. This, together with the whole of the *epidermis*, is separated from the *corium* by an exceedingly fine membrane, called the hyaline or glassy layer. It is this which forms the very thin buff-coloured "grain" surface of tanned leather, which evidently is of different structure from the rest of the *corium*, since, if it gets scraped off before tanning, the exposed portion of the *pars papillaris* remains nearly white, instead of colouring. The whole

of the hair-sheath is enclosed in a coating of elastic and connective-tissue fibres, which are supplied with nerves and blood-vessels, and form part of the *corium*. Near the opening of the hair-sheaths to the surface of the skin, the ducts of the sebaceous or fat glands (*e*, Fig. 30) pass into them, and secrete a sort of oil to lubricate the hair. The glands themselves are formed of large nucleated cells, arranged somewhat like a bunch of grapes; one is shown highly magnified in Fig. 36. The upper and more central cells are most highly charged with fat, which is shown by the darker shading.

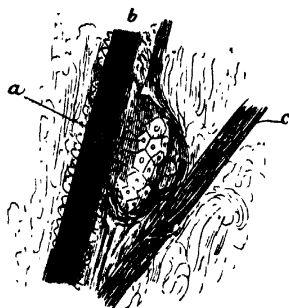


FIG. 36.—*a*, Sebaceous gland; *b*, Hair-stem; *c*, part of *erector pili* Muscle.

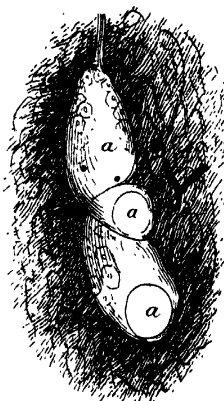


FIG. 37.—*a*, Windings laid open in making section.

As already remarked, the sudoriferous or sweat-glands are also derived from the epidermis layer. They are shown at *f*, Fig. 30, and on a larger scale (200 diam.) in Fig. 37 and also in Figs. 33 and 34; they consist, in the ox and sheep, of a large wide tube, somewhat convoluted, and with thin walls; while those of man form a spherical knot of extremely convoluted tubes. The walls of these glands are formed of longitudinal fibres of connective tissue of the *corium*, lined with a single layer of large nucleated cells, which secrete the perspiration. The ducts, which are exceedingly narrow, and with walls of nucleated cells like those of the outer hair-sheaths, sometimes open directly through the epidermis, as shown at *g*, Fig. 30, but more frequently into the orifice of a hair-sheath, just at the surface of the skin. Each hair is provided with

a slanting muscle (*h*, Fig. 30), called the *arrector* or *erector pili*, which is contracted by cold or fear, and causes the hair to "bristle," or stand on end; by forcing up the attached skin, it produces the effect known as "goose-skin." This muscle, which is of the unstriped or involuntary kind, passes from near the hair-bulb to the epidermis, and just under the sebaceous glands, which it compresses.

Beside the hair and hair-sheaths, and the sebaceous and sudoriferous glands, the *epidermis* layer produces other structures of a

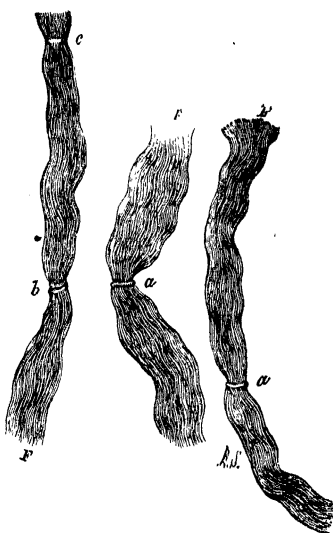


FIG. 38.—CONNECTIVE TISSUE FIBRES.

horny character, such as horns, hoofs, claws and finger-nails; which both chemically and anatomically are very analogous to exaggerated hairs, such as we have in the quills of the porcupine.

The *corium* or true skin is principally composed of interlacing bundles of white fibres, of the kind known as "connective tissue"; these are composed of fibrils of extreme fineness, cemented together by a substance somewhat different to the fibres themselves (*coriis*). This may be demonstrated by steeping a small piece of hide for some days in a stoppered bottle in lime-, or

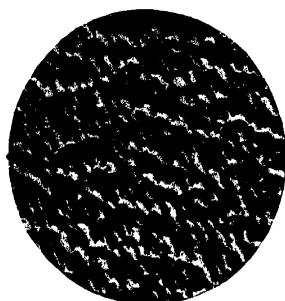
water, in which the interfibrillar substance is soluble, and then teasing a small fragment of the fibre with needles on a glass microscope-slide, and examining with a power of at least 200-300 diam.* In the middle portion of the skin, these bundles of fibre are usually somewhat loosely interwoven (and this is specially so in the sheep, where this part is also full of fat-cells). The outermost layer, just beneath the epidermis, is exceedingly close and compact, the fibre-bundles that run into it being separated into their elementary fibrils, which are so interlaced that they can scarcely be recognised. This is the *pars papillaris*, and forms the lighter-coloured layer, called (together with its very fine outer coating) the "grain" of leather. It is in this part that the fat-glands are embedded, while the hair-roots and sweat-glands pass through it into the looser tissue beneath. It receives its name from the small projections or *papillæ*, with which its outer surface is studded, and which form the characteristic grain of the various kinds of skin.†

The surface next the flesh is compacter than the middle part of the skin, and from the fibres running nearly parallel with the surface has a more or less membranous character. The skin is united to the body by a network of connective tissue (*panniculus adiposus*) which is frequently full of fat cells, and is then called adipose tissue. This constitutes the whitest layer, which is removed, together with portions of actual flesh, in the operation of "fleshing." If a minute portion of adipose tissue be examined microscopically, it will appear to consist of a mere mass of fat-globules (see p. 419) entangled in connective tissue. If, however, be stained with carmine or log-wood (p. 423), it will be at once recognised that each globule is contained in a cell, of which the nucleus and protoplasm, by which the fat was secreted, is pressed closely against the wall. Hence, in leather manufacture it is impossible to expel or wash out the fat till the cells have been broken down by liming or in some other way.

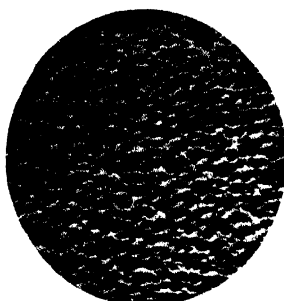
Many animals (ox, horse, etc.) possess a thin layer of volun-

* This solution of the cementing matter, and separation of the fibres is one of the most important results of the ordinary liming process of the tanner.

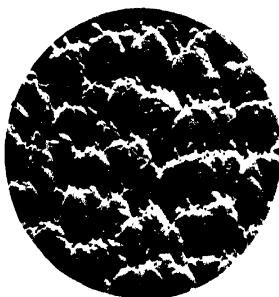
† It will be noted that the word "grain" is used by the tanner in at least three senses, which are productive of much confusion. The extremely thin hyaline layer forming a natural glaze to the skin, and might well be spoken of as such; the formless arrangement of the *papillæ* and hair-orifices might be called the "pattern" of the grain, and the word "grain" itself restricted to the *pars papillaris*.



1. Cow-hide,



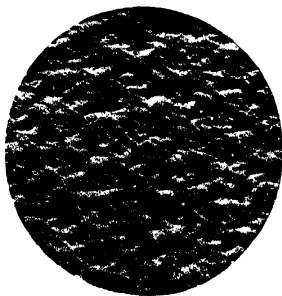
2. Calf-skin,



3. East India goat.



4. Pig-skin,



5. East India sheep.



6. Welsh sheep.

• GRAIN SURFACE OF LEATHER. (Magnified.) (A. Seymour-Jones.)

tary muscle (red flesh) spread over the inner side of the skin, and used for twitching to drive off flies. In rough fleshing this is sometimes left on, and may be the cause of dark flesh in sole-leather. Even in the finished leather its striped structure may be detected microscopically.

Besides the connective tissue fibres, the skin contains a small proportion of fine yellow fibres, called "elastic" fibres. If a thin section of hide be soaked for a few minutes in strong acetic acid, or the mixture of acetic acid and glycerin mentioned on p. 421,

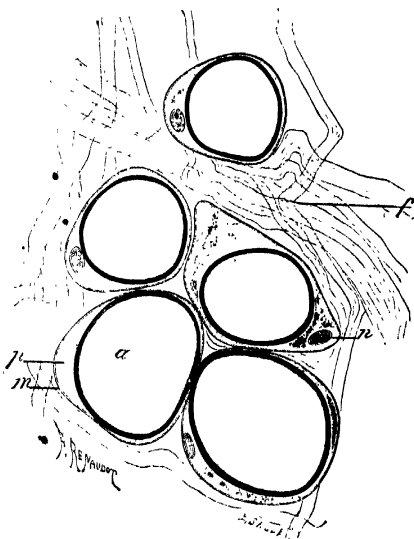


FIG. 39.—FAT CELLS IN CONNECTIVE TISSUE.

and then examined under the microscope, the white connective-tissue fibres become swollen and transparent, and the yellow fibres may then be seen, as they are scarcely affected by the acid. The hair-bulbs and sweat- and fat-glands are also rendered distinctly visible.

The nerves of the skin are very numerous, each hair being supplied with fibres passing into both the papilla and sheath. They also pass into the skin papillæ. They cannot readily be seen without special preparation, and, so far as is known, exercise

no influence on the tanning process. "Breaking the nerve" is a technical term, which signifies a thorough stretching and softening of the skin, but has nothing to do with nerves properly so called. The blood- and lymph-vessels are, from the present point of view, somewhat more important. They may often be seen in sections, and are lined with nucleated cells, similar to those of the glands. These are surrounded by coatings of unstriped muscular fibre, running both around and lengthways, and also by connective-tissue fibres. In the arteries, the muscular coating is much stronger than in the veins.

It may be thought that the space devoted to a discussion of the anatomical structure of the skin is disproportionately large; but there can be no doubt that, in order to make improvements, nothing is of more importance than a clear conception, even to the smallest details of the materials and causes to be dealt with. This can only be obtained by actual study of the hide structures with the microscope.

For general details of the methods of microscopic work, the reader is referred to Sect. XXIV.

But little useful observation can be made with the microscope on leather in an unprepared condition. On examining the "grain" surface of the leather with a low power and by reflected light the arrangement, number and position of the hair pores can be easily seen, and form distinctive marks of different kinds of skin, even in the finished state, when recognition in other ways is very difficult.

Scratches and the coarser kind of injuries to the grain surface may similarly be seen by reflected light, and an examination of the section, or "cut," will also give some idea of the tannage and of the presence of weighting matters. Thoroughly tanned leather shows masses of dark shiny substance between the fibres, while in undertanned leather these interspaces are empty and the fibres are usually more transparent.

Crystalline weighting matters, such as sugar and barytes, may often be seen mechanically lodged between the fibres, and in the pores from which the hairs have been removed.

Detailed study of the tanning process generally requires observation of the minute structure of the skin and epidermis, and of the changes which take place under the influence of manufacturing processes. Practically this is only possible upon

very thin sections, cut with a razor or section knife after hardening the hide with alcohol or some other reagent; but if it be required for technical purposes to make a rapid but rough examination, as, for instance, in order to show how far the cellular structures of the hide, such as hair-sheaths and fat-glands, are affected or destroyed in any stage of liming or bating, the following ready method may be employed. If a strip of hide cut $\frac{2}{3}$ through from the grain side, as shown at *a* in Fig. 40, and the flap be turned down and held between the finger and thumb, the fibrous tissue will be put on the stretch, and will then allow a moderately thin shaving (including the grain and parts immediately below it) to be cut by a sharp razor. The hide should be held in the positions shown, and a steady drawing cut be made from flesh to grain, the razor being steadied on the tip of the forefinger, and its hollow surface flooded with water, or a mixture of water and alcohol.

If the thin section be now placed on a glass slip, moistened with a drop of water, or with strong salt solution, which will render the fibre more distinctly visible, and examined on the microscope under a strong light from above with a 1-in. objective, the fat-

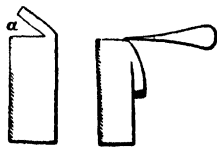


FIG. 40.

glands will be seen as yellow masses, embedded in the white fibrous tissue. If instead of salt solution a drop of a mixture of equal vols. of strong acetic acid, glycerin and water be used to moisten the section, the fibrous tissue will become quite transparent, and whatever remains of the cellular epidermis structures will be easily visible, and may even be studied under tolerably high powers if covered with a thin glass and lighted by the mirror from below. (The cover-glass must be carefully cleaned by rubbing with a linen handkerchief, and placed in position with a pair of forceps, one side being supported by a needle, which is gradually withdrawn, so as to avoid air-bubbles.) Care must be taken that the acid mixture does not touch the brass-work of the microscope; and even the vapour is apt to tarnish, so that the preparation must not remain longer than necessary on the microscope. The same method is applicable for ascertaining the completeness of the tannage of leather, and to decide whether the hide fibre is really tanned, or only dyed. Actually tanned

leather is only affected by the acetic acid when concentrated, or on long exposure, but raw or only stained hide swells and rapidly becomes translucent.

To prepare the very thin sections necessary for detailed study of the hide, more complicated methods are required. They may be cut after soaking the tissue in a strong solution of gum arabic, or even without previous preparation, by the freezing microtome; but are very tender and difficult to mount, and, in general, chemical treatment is preferable. Small slips of hide, not exceeding $\frac{1}{4}$ inch wide, and cut exactly across the lie of the hair, are placed first in weak alcohol (equal parts methylated spirit and water), and, after a few hours, are removed into strong methylated spirit, which must be repeatedly changed, until the hide is hard enough to give fine shavings. If the spirit is not strong enough to accomplish this in 24-48 hours, it must be replaced at the last change by "absolute" alcohol. It is desirable to cut as soon as the tissue is sufficiently hardened. This is best done with free-hand, as described on p. 403, and, if small or thin, the piece may be held between cork or pith, or embedded in paraffin wax (p. 403). The razor must be wetted with alcohol, and the section be made exactly in the plane of the hair-roots, which may be seen with a hand-lens. The use of a microtome for hide-sections is rarely satisfactory, as it is almost impossible to fix the fragment of hide so that it is cut exactly with the hairs, but it is sometimes useful when very thin sections are required for the study of details.

It is impossible to cut the sections too thin, and the student must be satisfied at first if they show here and there some of the structure distinctly. They should be floated off the razor into a basin or saucer of water by the aid of a camel's-hair brush, as they are very tender. After cutting a good number, those which are thick or defective may be fished out with a needle and rejected; but it must be remembered that torn sections are usually the thinnest and often show the most detail. The sections may now be stained by transferring to a saucer of picrocarmine * solu-

* Picrocarmine (and other staining solutions) may be bought of microscopic dealers, or prepared as follows (Rutherford's formula):—Heat 100 c.c. of cold saturated solution of picric acid to boiling, and add 1 gm. of carmine previously dissolved in a few c.c. of dilute ammonia by heat. Evaporate to dryness on the water-bath, dissolve in 100 c.c. of water, and filter. If the solution is not nearly clear before filtering, add more ammonia and evaporate a second time.

tion, the bottom of which is covered by a piece of filter paper, so that the fluid acts from below as well as above. If it is used of full strength, 15-30 minutes will suffice, but in many cases more characteristic staining will result from the use of a diluted solution for a longer time, which may extend even to 24 hours. The same remarks apply to the use of other stains, such as carmine, logwood and some of the aniline colours; but for further details of application, histological and microscopical works must be consulted. If picrocarmine be used, the connective tissue fibres (gelatinous fibres) and the nuclei of the cells will be coloured red, and the cells themselves of both epidermis and glands, together with the muscles and elastic fibres, will be yellow. The transference of sections from one liquid to another is frequently accomplished with a camel's-hair brush, but a section-spoon, made of thin copper or German silver, is less liable to tear them. The blade should be pierced with small perforations, which allow the liquid to run through the spoon and render the section much easier to catch.

The further treatment of the section depends on whether it is wanted for permanent preservation, or merely for examination. In the former case, it is generally best to mount in dammar varnish or Canada balsam. For this purpose it must be freed from water by soaking for an hour or two, first in dilute, and finally in absolute alcohol, to which some picric acid must be added if it is desired to retain the yellow staining of the picrocarmine. This not only dries, but hardens the sections, so that by the use of a camel's-hair brush they can be easily placed on the clean glass slip on which they are to be mounted. Superfluous alcohol is removed with blotting paper, and a drop of oil of cloves is placed on the preparation, which will soon make it so transparent that an unstained object becomes almost invisible. In this state it can be covered with a thin glass, and examined under the microscope to see if it is worth final mounting. When sufficiently cleared, the clove oil is sucked up with blotting paper, a sufficient drop of varnish is put in its place, and the cover-glass gently laid on with a needle (p. 421). The slide must be kept in a horizontal position for some months at least until the varnish has thoroughly hardened, when, if desired, superfluous drops can be scraped off with a knife, and the slide ringed with black japan; but this is more a matter of appearance than necessity. Canada

balsam dissolved in chloroform or xylene is frequently employed, but on the whole, solutions of gum dammar in benzene, xylene or turpentine are to be preferred. All these can be bought ready prepared, but dammar varnish is easily made by dissolving clear selected pieces of the resin in the required solvent to about the consistence of castor oil. Xylene solutions are now much used in bacteriological work.

For temporary examination only, the section, after a wash in water, which must be only slight if it be desired to retain the picric acid stain, is placed on the glass slip, and covered with a drop of glycerin and a cover-glass, when it will gradually clear as in the clove oil. It is possible to mount permanently in glycerin by painting round the edge of the cover with a ring of black japan, but the least trace of glycerin on the slide or edges of the cover prevents the proper adhesion of the japan, and leads to leakage and the ultimate destruction of the preparation.

An easier plan is to use Farrant's solution to replace the glycerin, in precisely the same way as the dammar varnish replaces the clove oil. This solution consists of 10 grm. of picked clear white gum arabic, dissolved without heat in 10 c.c. of distilled water and 5 c.c. of pure glycerin, a small lump of camphor or a fragment of thymol being added as an antiseptic. This solution gradually hardens round the edge of the cover, and can then be ringed with japan without difficulty. Another preparation is "glycerin jelly," which is gently warmed till it is melted, and applied on the slightly warmed slide in the same way as the Farrant's solution. It is best bought ready for use, as its preparation is troublesome.

Kathreiner, who made very elaborate researches on skin and the changes which take place in it during the processes of tanning, employed a mixture of osmic and chromic acids for hardening, and at the same time staining the tissue. This mixture was first used by a German histologist, Walther Flemming,* in a research on the internal organs of hearing, and was applied by Kathreiner in 1879 to the investigation of skin, and communicated by him to the writer in the autumn of that year. His method is briefly as follows. The pieces of hide, to be examined must, if salted, be well washed, or if dry, be thoroughly

* Some account of his work is given in Dr. Fischer's "*Fixirung, Faerbung und Bau des Protoplasmas.*"

softened. For the study of hide in its unaltered and natural condition, it is essential that it be quite fresh, and taken from the animal as soon as possible after death. In any case the *panniculus adiposus* or fatty layer is, as far as possible, removed with scissors, the hair cut short, and the skin cut up into little pieces of 3-4 mm. wide by 10-12 mm. long (about $\frac{1}{8}$ in. by $\frac{1}{2}$ in.); the hair must lie exactly across these pieces.

They are then placed for 4-8 days, according to the thickness of the hide, in about 12 times their volume of a solution consisting of

0.2 parts osmic acid ; *
 0.5 „ chromic acid ;
 200.0 „ water.

This solution must be kept from dust and light, in a glass stoppered bottle, and in a cool place. On removing the hide-pieces from this solution, they are placed in about 12 times their volume of absolute alcohol for 4-8 days, during which time the spirit must be at least three times renewed. The sections are cut with a razor flooded with absolute alcohol, so that the thin shavings float without friction upon it. The hide-pieces may be held either between soft cork, or, as is generally preferable, simply between the forefinger and thumb as shown on p. 403. The cut must be made exactly parallel with the direction of the hair-roots, and from the grain towards the flesh ; and the sections cannot possibly be too thin. After lying for $\frac{1}{2}$ -1 hour in absolute alcohol, the sections are soaked till quite clear in clove oil (which must be pale and of the purest kind), and may then be mounted in dammar varnish, or solution of Canada balsam.

In these sections, fat and oily contents of the fat-glands are stained black, and the limits of the cells both of these glands and of other elements of the hide (*rete malpighi*, hair-bulbs, etc.) are made very distinct, so as to be capable of the most delicate investigation under the highest powers ; though the beginner will learn most easily to recognise the different tissues by studying at first some sections stained with picrocarmine as before described. The method is admirably adapted for the study of hides as affected by the limes and bates.

⚠ Solution of osmic acid is best preserved in sealed tubes in the dark. If obtained in solution it is rarely of full strength, for which allowance may have to be made. Care must be taken to avoid inhaling its fumes, which are very irritating to the eyes and to the respiratory organs, producing severe catarrh.

Solutions of chromic acid (5 grm. per liter); of potassium or ammonium bichromate (50 grm. per liter), and of a mixture of 20 grm. potassium bichromate and 10 grm. sodium sulphate per liter (Müller's fluid) are frequently used for hardening tissues. A large volume (say at least 200 times that of the tissue) is required, and a time of six or eight weeks. A partial hardening in these fluids may be followed by one in alcohol of moderate strength, in which the tissue may be kept till required. Tissues hardened with chromic acid stain slowly, and somewhat differently to those treated simply with alcohol.

In place of the treatment with alcohol and clove oil, described on p. 423, sections may be dehydrated with alcohol, beginning, in the case of delicate tissues, with 10 per cent., and gradually rising to absolute, and finally to a mixture of equal parts of alcohol and xylene, which is replaced with pure xylene instead of clove oil, and finally mounted with a xylene solution of gum dammar or Canada balsam. Cedar-wood oil, or even turpentine, may also be used in place of clove oil.

The osmic acid of the solution described on p. 425, stains fats black by reduction, but another staining agent sometimes used for fats is made by mixing equal parts of water and solution of alkannin (the colouring matter of alkanet) in absolute alcohol, and afterwards filtering. This solution stains fats and oils, as well as essential oils and resins an intense red, while it affects other substances very little.

Professor T. Palmer* gives very detailed directions for the staining of sections of partially tanned leather so as to colour the tanned portions green, and the untanned red. For details, the original article must be consulted.

For other staining methods, Squire's 'Methods and Formulæ,' mentioned at the beginning of Sect. XXVI. may be consulted.

* Collegium, 1902, pp. 325, 331.

SECTION. XXVI.

BACTERIOLOGY AND MYCOLOGY.

FROM what has been said upon bates, drenches and liquors, it will be seen that the detailed study of bacteriology is of great importance in leather industry, and it would therefore be improper to omit all mention of its methods. The *technique* of bacteriology has, however, become so complex and highly developed that only a slight sketch of general methods can be given, and for the working details necessary to systematic research the reader is referred to the manuals devoted to the subject, among which the following may be specially mentioned :—

- Andreasch, 'Gährungserscheinungen in Gerbbrühen.' Vienna, 1827 ; and 'Gerber,' 1895-7.
- Dr. Rudolf Abel. 'Taschenbuch für den bakteriologischen Praktikanten.' A. Stubers Verlag, Würzburg.
- G. Günther. 'Bakteriologie.' Thieme, Leipzig (specially for microscopic technique).
- W. Migula. 'System der Bacterien.' Fischer, Jena.
- J. Curtis. 'The Essentials of Practical Bacteriology.' Longmans, London.
- F. Lafar. 'Technical Mycology.' Griffin. London.
- Slater and Spitta. 'An Atlas of Bacteriology.' Scientific Press, London.
- P. W. Squire. 'Methods and Formulæ used in the Preparation of Animal and Vegetable Tissues for Microscopic Examination, including the Staining of Bacteria.' Churchill, London, 1892.
- Reynolds Green. 'Soluble Ferments and Fermentation.' Cambridge University Press.

Bacteria, yeasts, and to a less extent other fungi, together with some of the lowest forms of animal life (monads), are the cause of those changes which are classed under the general terms of fermentation and putrefaction, the latter word being generally applied to those forms of fermentation of nitrogenous, and especially of animal substances in which unpleasant odours are produced. For the sake of clearness, it is therefore necessary to say a few words here on the general nature of fermentation,

though the subject has been more fully dealt with in the Author's 'Principles of Tanning.' It must not be supposed that all fermentation is directly caused by actual living bacteria and yeasts. In animals and the higher plants, substances are broken up for purposes of nutrition, and the production of heat and energy, partly by oxidation and partly by the absorption of the elements which are required for building up the organism, while the unnecessary constituents are rejected. These processes are identical in principle with those carried on by yeasts and bacteria, the only difference being that in the latter case the acting cells form part of a more complex organism, while in the former they are independent and disunited. In the case of green plants, all the carbonaceous nourishment is obtained from the carbonic acid of the atmosphere, which, under the influence of sunlight, is reduced by the green colouring matter (chlorophyll), to formaldehyde, or some allied substance which condenses to form sugars, starch, and other carbohydrates. The organisms of fermentation, on the other hand, possessing no chlorophyll, have to obtain all their nourishment ready formed from already existing animal or vegetable matter, which they must have the power of liquefying or digesting, since, in general, they have no means of absorbing solids. In the higher plants and animals many processes go on which we often call 'digestion,' but which might properly be classed as fermentation, which are not caused directly by the cells themselves, but by substances secreted by them. Thus, in animals the saliva contains a substance, ptyalin, which converts starch into glucose, and in sprouting seeds (e.g. malt), diastase is formed which has similar functions. Digestion of flesh and albuminous substances is caused in the stomach by pepsin, and in the intestines by trypsin (or pancreatin), both of which have the power of liquefying not only gelatin but coagulated albumin and fibrin; and in the vegetable kingdom analogous bodies exist with similar powers. These substances are called zymases, enzymes, or "unorganised ferments"; and are allied to the albumins, and, like them, coagulated and rendered inactive by heat. They are also precipitated by strong alcohol, but in this case regain their activity on being redissolved in water. The most curious fact about them is, that very small quantities seem capable of fermenting almost unlimited amounts of the substances on which they act, without themselves undergoing permanent change.

The mechanism of this is not clearly understood, but is allied to what have long been known as "catalytic" action in inorganic chemistry, which is generally defined as the power of substances to hasten reactions which tend to take place, but in which the catalysing substance takes no permanent part. Hence, such actions do not, as in the case of chlorophyll, draw upon any outside energy, but consume a part of that already stored in the material acted on, and consequently they result, not in building up, but in pulling down, reducing complex materials to simpler forms containing less stored up energy. This indeed applies to all actions of bacteria and yeasts, though in some cases a small portion of complex matter is built up by the destruction of much matter of a simple sort.

It is now known that bacteria and yeasts frequently secrete zymases, and that many of the changes they cause are due to the action of these bodies, and not to the direct effect of the cells themselves. The separation of zymases from the bacteria is not easy, since by heat both are destroyed; but while the bacteria are paralysed by ether and chloroform, the zymases are not affected; and in other cases the bacteria may be removed by filtration through compact earthenware (Chamberland "candle"), while the zymases pass through. The zymases may then be precipitated by alcohol, and obtained in a state of approximate purity. Wood has shown that the starch of bran must be converted into sugar by a zymase, cerealin, contained in the bran, before it can be fermented by the drench ferment (p. 94), and that the liquefaction of gelatin and hide fibre is caused not by the direct action of bacteria, but by zymases which they secrete, to which principal effect of bates and drenches is due. Such zymases are also undoubtedly present in old limes and putrid soaks.

While most plants, as well as animals, are dependent on the oxygen of the air, which, by oxidising the carbon and hydrogen they contain, provides them with heat and chemical energy, many bacteria are independent of free oxygen, obtaining all they need from the materials forming their nourishment, and some cannot even subsist in presence of free oxygen. Bacteria are thus classified into *aerobic* which use free oxygen, and *anaerobic* which do not. As the anaerobic bacteria take oxygen from the compounds on which they feed, their products are "reduced," or

contain less oxygen than the original substance, and hence they tend to produce such bodies as amines and sulphur and phosphorus compounds such as SH_2 , which are frequently evil smelling and sometimes very poisonous, as in the case of ptomaine-forming and many pathological bacteria. Aerobic or oxidising bacteria, on the other hand, tend to convert their nutriment into such simple compounds as carbonic acid, water, and nitrogen or ammonia, and hence their final products are harmless and often inodorous. This property is now largely made use of in the purification of sewage by "contact beds" containing immense quantities of oxidising bacteria, frequently after a previous treatment by anaerobic bacteria in "septic tanks," in which the solid matters are broken down and dissolved, and simpler compounds, better adapted to the aerobic bacteria, are produced. It often happens, as in this case, that fermentive changes are produced by a series of bacteria, each carrying the matter through but one stage of the process, and dependent on their predecessors for their proper form of nourishment.

Classification of Bacteria.—Bacteria belong to the class of *Schizomycetes* or fission-fungi. They multiply by lengthening and subsequent division, but the rod-forms frequently produce a spore at one end, which subsequently develops into a new rod. The spores are generally much more resistant to heat and antiseptics than the perfect organism. Our knowledge of Bacteria is still too imperfect to render possible any complete classification based upon their structure and habits, but for practical purposes they are generally divided into four groups as follows:—

Micrococcus.—Small spheres, either free or joined in chains, having the appearance of a string of beads.

Bacterium.—Oval, dumb-bell shaped, or very short rods, often classed with *bacillus*.

Bacillus.—Rods, sometimes joined in chains, frequently motile.

Spirillum.—Spiral or corkscrew-shaped rods, which very often move rapidly through liquids, rotating like a screw.

The distinction, however, between these forms is not always well marked. *Bacilli* and *Spirilla* frequently produce spores which at first are like *micrococci*, and bacteria of all stages of length between the elongated rod and the purely spherical form

are known to exist. Not unfrequently a dumb-bell shaped form is seen, which may consist either of bacillus with somewhat enlarged ends, or may be simply a developing micrococcus in which the sphere is lengthened, and is about to separate into two individuals.

The division of these classes into species is difficult, and in many cases very uncertain, since the organisms are too small for us to observe any internal structure by ordinary means, and it frequently happens that bacteria of apparently identical form and size produce very different effects of fermentation or disease. It is therefore usually necessary for any certain identification to obtain a pure culture, and to ascertain its chemical or physiological effects; but many bacteria may be distinguished by methods of staining which affect different species differently, and of which some particulars will be given on p. 448. Different species may frequently be identified by the microscopic appearance of cultures, in different solid media. As a whole, our knowledge of pathological bacteria is much more advanced than of those of fermentation, to which less attention has been paid; and it is therefore impossible to give particulars at all complete of the organisms which produce the various fermentations; and I shall only attempt here to describe a few of the principal and most completely identified forms. Further details may be found in the bacteriological treatises already mentioned. The matter is additionally complicated by the fact that the same products of fermentation are occasionally produced by very different bacteria, or even by yeasts and the lower forms of fungi, which are frequently present in liquors, and of which a few will be described for convenience sake at the end of the section on bacteria.

There are undoubtedly living organisms (mostly bacteria) of smaller dimensions than can be seen by the most powerful microscope. Their existence may be rendered visible by means of the ultra-microscope of Siedentopf, in which, by special means of illumination, particles of less diameter than a wave length of light are seen by the light they reflect—*vide* H. Siedentopf on the rendering visible of the ultra-microscopic bacteria.*

Bacteria are frequently divided into "aerobic" which thrive in presence of air or oxygen, which is consumed by them in

Journ. Roy. Micro. Soc., 1903, 576; also N. Gaidukov, Centr. Bl., xvi., 781.

oxidising the media on which they subsist (like animals); and "anaerobic," which only exist in absence of free oxygen, and derive their energy from breaking down existing compounds. Many bacteria can exist under both conditions, varying their fermentation-products, and frequently their form and development accordingly.

The following descriptions are taken from various authorities, supplemented by information given by Mr. J. T. Wood, who has kindly revised the section. The size of the bacteria are expressed in μ (micromillimeters, or thousandths of a millimeter). For more detailed descriptions, original papers, and the larger bacteriological text-books must be consulted.

MICROCOCCUS (spherical or slightly oval cells).

M. flavus liquefaciens, found in air and water, produces yellowish colonies rapidly liquefying gelatine. The cells are large, found in pairs or in small masses.

M. (or Bacillus) prodigiosus, found in air, liquefies gelatine rapidly; colonies form bright red spots. Cultures smell of trimethylamine. Cells spherical or oval, of a diameter of 0.5μ or more to $1 \times 1.7 \mu$. Grows on bread and other foods. *Prodigiosus* is generally classed among bacilli in the text-books, although in appearance it is very like a micrococcus.

M. ureæ, spherical, 1 to 5μ in diameter, generally in long chains. Ferments urea and liquids containing it, producing ammonium carbonate and carbamate. Does not liquefy gelatine. The colonies are white, like drops of stearin. Several other bacteria are capable of fermenting urea.

Micrococcus ureæ liquefaciens (Flügge) $1.25-2 \mu$ in diameter, single, or in little chains or irregular groups, liquefies gelatine slowly.

Leittonostoc mesenteroides (Cienkowski), a small spherical bacterium, which produces large gelatinous masses or zooglae in which it is embedded. It is very common in the liquors of beet-root sugar-works, rendering the liquors viscid by the production of a substance allied to cellulose, and causing much trouble both in this way and by choking pipes.

Ascococcus Billrothii is a very similar organism to the last, producing butyric acid, together with a viscous fermentation of sugars.

The majority of bacteria germs found in the air are micrococci, especially species of *sarcina*, of which a large number of varieties have been found (see Th. Gruber, 'Die Arten der Gattung *Sarcina*, Centr. Bl. für Bakt. Zweite Abth. i. 588). The commonest form is *Sarcina ventriculi* (Goodsir), which occurs in little packets of eight micrococci.

BACILLUS (elongated or rod-shaped bacteria).

1. *B. aceticus* (or *Bacterium aceti*) (*Mycoderma aceti* Pasteur). Short rods about $2\ \mu$ long, but very variable. Motile when free, but generally forming tough skins of gelatinous matter (zoogloea) called "mother of vinegar." Ferments weak alcoholic solutions into acetic acid in presence of air. Compare Brown, 'Journ. Ch. Soc.,' 1886, p. 172, who states that at least two other bacilli cause acetic fermentation. A full account of the three acetic acid bacteria is given by Hansen, 'Recherches sur les Bactéries Acétifiantes,' Centr. Bl. für Bakt. Zweite Abth. i. p. 31.

2. *B. butyricus* (Fitz). Rods, $3-5\ \mu \times 0.6-0.8\ \mu$. Very mobile, produces spores larger in diameter than the rods. Ferments carbohydrates into butyric acid in absence of air, evolving also much H and CO_2 .

On butyric fermentation compare Ed. Baier, 'Ueber Butter-säuregährung,' Centr. Bl. für Bakt. Zweite Abth. i. p. 17; and Beyerinck, 'Ueber die Butylalcoholgährung und das Butyl-Ferment,' Amsterdam, 1893. The latter finds that a large number of species produce butyric acid in absence of oxygen, and at the same time secrete granulose, which causes their cells to stain blue with iodine. Hence Beyerinck adopts *granulobacter* as a name for the whole class, and his *G. saccharo butyricum* is probably identical with *B. butyricus* (Fitz). *B. butyricus* (Hueppe), $2.1\ \mu \times 0.38\ \mu$, appears to correspond with *G. polymyxa* (Beyerinck). All these bacteria evolve H and CO_2 vigorously, as well as alcohols, butyric acid being by no means the principal product, even in pure cultures. *Bacillus butyricus* (Prazmowsky) is the *Clostridium butyricum*. The spores are $1\ \mu$ broad and $2\ \mu$ long.

Hueppe isolated an *aerobic* bacillus from milk, which liquefied gelatine and formed butyric acid.

Baier's paper is still the best account of butyric fermentation but latterly an immense amount of work in the bacteriology of

cheese ripening, by Freudenreich and others in Europe, and Conn in America, has resulted in the isolation of several new species of butyric bacteria. The literature, both of this and lactic fermentation, is now so vast that it is impossible even to give a clear résumé of it here. In Centr. Bl. 2 Abth. xvi. (1906), Adolf Reitz gives a bibliography of this literature (13 closely printed pages).

B. lacticus. Short rods, $1.7 \mu \times 0.6 \mu$, not motile, anaerobic. Does not liquefy gelatine, but forms colonies of a greyish white. Causes lactic fermentation of sugars, and coagulates milk in 15–24 hrs. at 30°C . Compare Kayser, 'Études sur la fermentation lactique,' Ann. de l'Inst. Pasteur, 1895, p. 737. Henneberg, Zeitsch. f. Spiritus Industrie, 22, 23, 1903, has published a very interesting research on the behaviour of 19 different species of lactic bacteria in milk, beer, pressed yeast, molasses, etc.

The most important fermentation process from the tanner's standpoint is lactic acid fermentation. There are a large number of organisms which ferment sugars with production of lactic acid, and unfortunately many workers have described and studied the same organism under different names. The principal organism causing the spontaneous coagulation of milk is that described by Leichmann as *B. lactis acidi*. This organism and varieties of it have been described by different authors under the names of *Streptococcus acidi lactici* (Grotenfelt); *B. acidi lactici* (Gunther); *B. lactis acidi* (Leichmann); *B. lactari* (Dinwiddie); *Bacillus lacticus* (Freudenreich); vide W. M. Esten, Centr. Bl. xvi., 536.

B. lactis acidi is a facultative aerobe. It does not form gas in saccharine liquids. It has an optimum temperature of 32° – 38°C ., and requires N in the form of peptones. It will not grow in a fluid with the N in the form of asparagine or ammonium sulphate. It may easily be distinguished from the *coli* bacteria, as it stains by Gram's method, whereas the *coli* bacteria do not. (Vide G. Leichmann, 'Ueber die freiwillige Säuerung der Milch,' Centr. Bl. ii. 2, 777).

The principal gas-producing lactic organisms are *B. coli commune* and *B. lactis aerogenes*, which are aerobic. Lactic acid bacteria are all non-motile, and do not form spores. Butyric acid bacteria nearly all form spores, and some possess flagella, and are motile.

Campbell states that practically pure cultures of *B. lacticus* are obtained by continued cultivation in milk.

It is stated that at least 15 distinct bacteria are known to produce lactic acid, CO_2 , and acetic acid being formed at the same time, with traces of formic acid, acetone and alcohol. The *B. acidi lactici* (Hueppe) is, next to *B. lacticus*, the most important lactic ferment.

B. lactis viscosus (Adametz) and *B. viscosus* (Frankland) have been identified by Andreasch as the principal ferments of "ropy" or viscous tanning liquors.

B. furfuris (Wood). See 'Journ. Soc. Ch. Ind.,' 1890, p. 27; 1893, p. 422; 'Brit. Ass. Rep.,' 1893, p. 723. The principal ferment of bran drench. Oval cells $1.25 \mu \times 0.75 \mu$, frequently found in pairs, dumb-bells or chains. Pure cultures do not attack hide, and only ferment the starch after it has been converted into glucose by cerealin, a zymase or unorganised ferment similar to diastase, and naturally present in the bran. The principal products of the fermentation are lactic and acetic acids, with traces of formic and butyric acids, hydrogen sulphide and trimethylamine, and considerable evolution of hydrogen and carbon dioxide. In one drench analysed, 0.24 grm. acetic and 0.79 grm. lactic acid per liter were present, and an artificial solution of 0.5 acetic and 1.0 lactic acid (sp. gr. 1.210) per 1000 produced in 1½–2 hours an effect on skin quite similar to that of an ordinary drench in 12–16 hours, and when tanned gave a satisfactory leather. (Cp. p. 94).

Wood* has isolated a second bacterium (*B. furfuris* β), very similar in appearance to the first, and taking part with it in the fermentation of ordinary drenches, which it somewhat modifies. No doubt in different tanneries differences exist in the character of the ferments present. When the skins themselves are attacked the effect is generally due to putrefactive bacteria brought in from the puers, etc., but these do not usually produce any effect till the glucose, which forms the nutriment of *B. furfuris*, is exhausted. In hot weather a butyric fermentation sometimes supervenes, when the skins become "glassy" and swollen, and are rapidly destroyed (see p. 434).

B. furfuris α and β belong to the group of *Coli* bacilli, and are capable of fermenting milk with production of lactic acid.†

B. mirabilis, *Proteus mirabilis* (Hauser). Mobile rods 2–3,

* 'Journ. Soc. Ch. Ind.' 1897, p. 510.

† On Manufacture of Lactic Acid, 'Journ. Soc. Ch. Ind.,' 1897, p. 516.

$\times 0.6 \mu$. Agent of putrefaction of animal substances. Aerobic, liquefies gelatine rapidly in presence of oxygen. Colonies on plates produce long tortuous prolongations.

B. vulgaris, *Proteus vulgaris* (Hauser). Almost identical with the above. Mobile rods $1.25 \mu \times 0.8 \mu$. Compare Hauser, 'Ueber Fäulnisbacterin,' Leipzig, 1885. *B. vulgaris* is the commonest putrefactive bacillus. *B. mirabilis* differs from the above chiefly in the mode of growth on solid culture media.*

Many putrefactive bacteria are capable of producing acids from sugar (*vide* Rahm, O., Centr. Bl., xiv. p. 22).

B. termo. Not now considered a distinct species, but comprises the two last and many other putrefactive bacteria.



FIG. 41. —*B. furfuris* a.

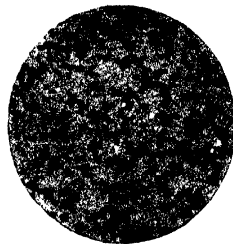


FIG. 42.—*B. furfuris* B.

B. ureæ. Slender rods, less than 1μ in diam. Can grow without oxygen. Causes ammoniacal fermentation of urea.

Wood has found in "puer" liquor *Proteus vulgaris* and *B. subtilis*, among others, and probably *Bacillus ureæ* (Cohn) and *M. fulvus*.

Thiothrix or *Beggiatoa*, sulphur bacteria. Long threads, living in waters containing sulphuretted hydrogen, and assimilating sulphur.

Beggiatoa alba. One of the most common. Threads dirty white, 2 or 3μ in diam., containing granules of sulphur, common in sulphur springs as well as in soak pits and other waters containing sulphuretted hydrogen as a product of putrefaction. There are several other similar species. Their life-history has been specially studied by Winogradsky.†

* For a short account of putrefactive organisms, see a paper by Wood, 'Journ. Soc. Chem. Ind.,' 1906, p. 109. See also Lafar, p. 741, 'Ueber Protein Faulniss.'

† 'Morphologie und Physiologie der Schwefelbakterien,' Leipzig, 1883.

SACCHAROMYCETES.

In addition to the true bacteria which act as ferments, there are certain other fungi which also have the power of producing fermentation; especially those belonging to the class of *Saccharomycetes* or yeasts, which are the cause of ordinary alcoholic fermentation, although certain true bacteria have the same power. The yeasts, unlike the true bacteria, multiply by budding or spores, and not by division. The different species of

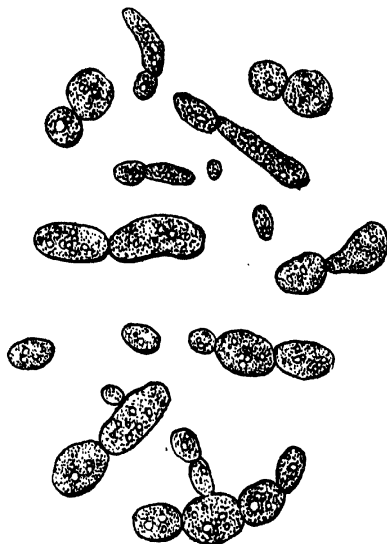


FIG. 43.—YEAST.

yeast vary in size, and are more or less round or elongated in form, but in general resemble the ordinary beer yeast closely in appearance, which may be conveniently studied in brewers' or German pressed yeast.

Saccharomycetes mycoderma is very frequent at the surface of tanning liquors, forming the thick and wrinkled scum which is familiar. The cells are usually oval or elliptic, but sometimes cylindrical, $6-7\ \mu \times 2-3\ \mu$, often forming thick and branched chains, and occasionally taking forms very similar to the hyphae

(see below) of the higher moulds. It was formerly supposed that it was an acetic acid ferment, but the true acetic acid ferment (see p. 434) is a bacterium frequently forming part of the scum produced by the mycoderma. It does not appear to produce alcohol in perceptible quantities, though it frequently causes a vinous odour, and, when freely supplied with oxygen, oxidises and destroys the acetic and other acids produced by bacterial fermentation.

There are several other species of mycoderma which are either identical or very closely allied to the above.

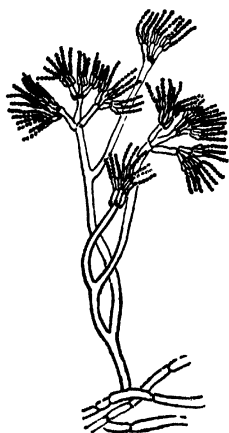


FIG. 44.—*Penicillium glaucum*.

A few species of *Saccharomyces* produce lactic acid, e.g. *Saccharomyces acidi lactici* (Grotenfelt). Andreasch has also isolated three species of yeasts from sour tan liquors which produce lactic acid.

The branching stems or hyphæ of the higher moulds, and especially of the mucors, appear to act as ferments when immersed in liquids, but the subject cannot be considered yet as being fully investigated. Van Tieghem ('Ann. d. Sc. Nat.,' Ser. 5, 1867, p. 210) showed that the mycelium, both of *Penicillium* and *Aspergillus*, when growing in a solution of tannin, breaks up the tannin into gallic acid and glucose. Although their study does not properly belong to the subject of Bacteriology, it will be convenient here to mention one or two which are sure to be encountered by the microscopist.

ASCOMYCETES (spores in tassels or heads unenclosed in sporangia).

Penicillium glaucum, green mould, the most common of the mould fungi, is shown in Fig. 44. In its earlier stages it consists of a mass of hyphæ or branched stems, composed of elongated cells, and forms a white mould. As it becomes developed it throws up stems, on the top of which the spore-bearing cells

(conidia) appear, which, under the microscope, have the aspect of a tassel of bluish-green beads. This is most easily seen by examining dry, as the tassels immediately break up in the presence of moisture into single spores, each of which is capable of producing a fresh plant. The spores are about 3.5μ and the mycelia from 0.7 to 4μ in diameter.

Aspergillus spores grow on short conidia clustered on a club-shaped head. *Aspergillus glaucus*, pale green or bluish spores.

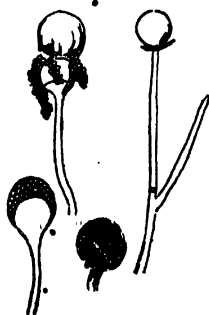


FIG. 45.—*Aspergillus*, showing spores, mode of conjugation, and eurotium form.

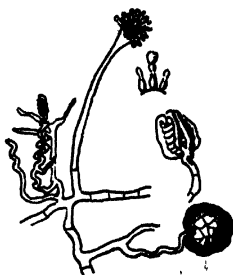


FIG. 46.—Fructification of *Mucor*.

A. niger (Fig. 45), a dark chocolate brown mould, which grows well on acid fruits and liquids.

This genus also produces large "resting spores" (*Eurotium*) by sexual fructification, which were formerly considered to belong to a separate fungus and known as *eurotium*.

PHYCOMYCETES (spores in membranous sporangia).

Pilobolus.—Hyphæ 1–2 mm. high, glassy tufts; occurs on excrement.

Mucor mucedo, white mould; hyphæ colourless, simple or branched, 1–15 cm. long; sporangia brown or black, thus distinguished easily from those of *P. glaucum* which are bluish-green (Fig. 46).

The moulds have much more destructive effect on tannins than the bacteria. Eitner* showed that the introduction of

* 'Gerber,' 1889, p. 2.

putrefaction bacteria into tan-liquors had no destructive effect on the tannins, and the same was proved by Kohnstein and Simand with regard to the lactic ferment. * On the other hand, it is well known that tannins are quickly destroyed by moulds; Wood † mentions that the tannin in a sterilised sumach infusion remained practically constant for 23 days, while in one infected with *Penicillium glaucum*, 80 per cent. of the total was destroyed in the same time.

Bacteriological Methods.—It is generally useless to attempt bacteriological work of any elaborate kind without a separate and properly fitted laboratory, from the air of which germs can be rigorously excluded; and therefore only a few simple methods of preliminary experiment which can be carried out reliably under ordinary conditions, will be here described. Cultures and inoculations may however be made in any ordinary laboratory, by providing a glass case with a sliding front like a balance case, but somewhat wider, the inside of which is wiped over with an antiseptic solution of carbolic acid and glycerine, and allowed to stand closed, until all germs have become deposited and adhere to the sides of the chamber; if it be then carefully opened inoculations, etc. may be made by opening the tubes or Petri dishes inside the case, just sufficient aperture being left for the insertion of the operator's hands. His sleeves should be turned back, and hands and wrists washed with carbolic soap or an antiseptic solution.

As every fermenting material contains, beside the organism producing the principal change, many others which are accidentally present, the first step in bacteriological work is to obtain what are called "pure cultures," containing one species of organism only. It is then possible to study the effects of this organism undisturbed by secondary fermentations, and to determine what products are actually due to it. Since all ordinary materials and objects are swarming with bacteria, a necessary preliminary to pure culture is to obtain liquids and apparatus absolutely sterile or free from living germs, and for this purpose various methods are employed according to the nature of the material to be dealt with.

Indiarubber stoppers, and other objects which will not stand a temperature of 150° C., may be sterilised by washing with a

* Gerber, '1886, p. 253.

† 'Journ. Chem. Ind.,' 1894, p. 221.

solution of mercuric chloride of 0.1 per cent., and afterwards rinsing with sterilised water. Chloroform and ether may be used for sterilisation of more delicate objects, and are easily driven off by heat, but are not very reliable, but useful as a means of checking the development of bacteria in liquids, without stopping the action of unorganised ferments or zymases (p. 429). Other chemical means of sterilisation may often be employed. N/4 NaOH solution will destroy most bacteria, and may be neutralised with an equal quantity of N/4 HCl, common salt only remaining, or the process may be reversed, mineral acids being also powerfully bactericidal. Hypochlorates, chlorine, or bromine, may also be used and removed or converted into inactive compounds by thio-sulphates or sulphites. Copper and mercury salts may be removed from liquids by SH_2 , and so on. Strong CaCl_2 solutions, or even prolonged salting, will kill many bacteria, and are easily removed by washing. These methods are often useful with hide or other tissues to which heat cannot be applied, when it is desired to sterilise them before submitting them to the action of other bacteria.

The most important means of sterilisation, however, is the employment of heat alone. Platinum wires and other objects not easily damaged may be held for a moment in the flame of a Bunsen burner; glass vessels and plates, cotton-wool and many other objects may be heated in an air-bath to 150°C ., or submitted to the action of steam at 110°C . (10 lbs. per square inch pressure) for half an hour. As steam under pressure, however, involves the use of special appliances, it is often more convenient to employ the lower temperature of steam at atmospheric pressure by which bacteria are killed in the course of an hour, though their spores are frequently much more resistant and need at least five or six hours for complete sterilisation. In many cases, as in the sterilisation of water and other liquids, it is preferable to heat for an hour to boiling point daily for three successive days, when the spores become developed and are killed by the later heatings. Sterilisation of liquids which are altered by boiling may be generally accomplished by heating daily for four or five hours to 60°C . for a week, though some few bacteria will thrive at this temperature. For the preliminary experiments which are likely to be undertaken in the tannery laboratory, an ordinary potato-steamer will be found to form a convenient steriliser for many purposes, and the air-bath of the laboratory heated to 150°C .

may also be useful. It is usual to plug the necks of flasks, test-tubes, and other vessels in which liquids are being sterilised, with cotton wool, which of course becomes sterilised at the same time. If from any cause the plug is withdrawn, as for instance to take samples of the liquid, it must be singed in the flame before it is replaced, in order to destroy any germs which have fallen upon it, and the vessel during the process must be held in an inverted or sloping position so as to lessen the danger of germs falling into the liquid; and it need hardly be said that the platinum wire or pipette, which is employed for drawing samples, must itself be thoroughly sterilised before use. Anaerobic bacteria may be cultivated by placing the culture tube inside a wider tube 3 c.m. \times 25 c.m., containing 1 grm. pyrogallol and 10 c.c. of a strong solution of caustic potash. The tube is then closed by an air-tight indiarubber stopper. They will also frequently develop in the lower part of solid media (gelatine, agar-agar) in test-tubes.

Various nutritive materials are employed for the culture of bacteria. In Pasteur's researches, liquids were generally used; but at present it is found convenient in many cases to employ solutions of gelatine or agar-agar, which at ordinary temperatures form a solid jelly. Many bacteria have the power of liquefying gelatine, probably by the production of a zymase; and to the leather manufacturer it is not without importance to distinguish these, as there can be little doubt that they are active in producing solution of the hide fibre.

Pasteur's original solution consisted of 1 grm. ammonium tartrate, 10 grm. crystallised sugar, and the ashes of 1 grm. of yeast, dissolved in 100 c.c. of water. Buchholz modified this nutritive solution by substituting 0.5 grm. of calcium phosphate for the yeast ashes. Cohn employed 0.10 grm. potassium phosphate, 0.10 grm. crystallised magnesium sulphate, 0.01 grm. tribasic calcium phosphate, 0.20 grm. ammonium tartrate and 20.00 c.c. of water. Many bacteria will live in these solutions, though they were originally designed for the study of yeasts and fungi.

Bacteria usually thrive much better in meat broths than in these saline solutions. An ordinary mode of preparation is as follows: 250 grm. of beef muscle carefully freed from fat is gently simmered for five hours in 1 liter of water, the fat as it rises being skimmed off. It is allowed to stand overnight in a

cold place, solidified fat is removed, and the liquid made neutral to litmus by dilute caustic soda solution. It is then again boiled for ten minutes, filtered through paper previously wet with water, made up to one liter and measured into experimental flasks or test-tubes, in which it is sterilised.

Many other nutritive solutions are employed, for the preparation of which the bacteriological text-books may be consulted. In many cases it is advantageous to cultivate bacteria in the medium in which they normally exist; thus, "drench" bacteria may be grown in a filtered and sterilised drench liquor, and the bacteria of bates, puers, etc., in their appropriate liquors similarly treated.

The methods of cultivation in gelatine are, as a rule, more easy to handle successfully in ordinary laboratories than those in liquids, and are therefore of special interest for technical use. A suitable jelly for this purpose may be made by dissolving 6-15 per cent. (according to temperature) of the finest French gelatine in the nutritive broth which has been described; or 1-2 per cent. of dry meat peptone (*peptonum siccum*), and if desired, 1 per cent. of pure glucose may be added to a simple solution of gelatine in water. These solutions may require to be neutralised with soda similarly to the meat extract, and must be purified by repeated filtrations. It is frequently necessary to clear with white of egg, in order to obtain perfectly bright solutions; this is done by adding to each liter the white of one egg, which has been previously beaten to a froth with a little water. The temperature of the liquid must not exceed 40°-50° C. when the egg is added, but is then raised to boiling point, or even heated to 110° C. or more to coagulate the albumen, which carries down with it all suspended matter, and may be removed by filtration through flannel or paper. The coagulation of the egg should always be performed at a temperature at least as high as that which will be afterwards employed in sterilising, or a further precipitation may take place during that process. Where somewhat high temperatures are required in cultures, agar-agar is substituted for gelatine, as its jellies have a higher melting point, but this will not often be required in tannery work. The jelly after filtration is usually sterilised in test-tubes, 5 or 10 c.c. being measured into each, and the tube plugged with cotton-wool.

The plugs should be of the pure cotton-wool used for medi-

cal purposes, tolerably light and compact, and covered during sterilising with tinfoil, to lessen the destructive action of the steam. For some purposes (roll-cultures, p. 445) small cylindrical bottles of clear glass, and especially the thin blown bottles used for oil samples, are to be preferred to test-tubes. Flasks and bottles with flat sides have also been used. Several dozen tubes or bottles may be sterilised at once by placing in a wire rack in the steamer, and steaming for an hour daily for three successive days. Properly sterilised tubes should remain clear and unaltered for an unlimited length of time, but though the cotton plugs exclude all germs, in an ordinary laboratory moulds are apt to develop on them, and in the course of weeks to grow through and infect the sterilised media. This danger can be lessened by covering the plugs, after singeing, with a rubber cap or even with tinfoil, but these will also exclude air, which is indispensable to the development of many bacteria.

Cultivation.—As it is extremely difficult to avoid the admission of germs from the air of an ordinary laboratory into nutrient liquids which are to be inoculated (see, however, p. 440), the employment of the nutrient gelatine will be first described. To inoculate this, a platinum wire (fused into a piece of glass tube) is usually employed, which may be either straight (needle), or bent into a loop (*Oese*). This is ignited for a moment in the flame to sterilise it, then allowed to cool, and dipped in the liquid containing the bacteria. A test-tube of sterilised gelatine is held in the left hand upside down, and the plug of cotton-wool is drawn out between the little finger and second finger of the right hand, and the platinum needle (which during this operation has been retained in the hand) is thrust into the gelatine almost to the bottom of the test-tube, quickly withdrawn, and the plug of wadding replaced, frequently after first singeing it in a flame.

In case of what is called "tube" or "stab" culture, the tube is now simply retained at a suitable temperature, which may vary according to the object of the experiment, from that of the laboratory up to anything below the melting point of the jelly. The bacteria multiply upon the sides of the prick, producing in many cases very distinctive appearances, some forms liquefying the gelatine and others spreading into it without liquefaction. Anaerobic bacteria only develop in the deeper parts of the tube, while aerobic are confined to the surface, while some species ("facultative" aerobic or anaerobic) can thrive

under both conditions. Some species of bacteria also produce brilliant colouring, or fluorescence. Illustrations of these static cultures may be found in most bacteriological text-books. This method, however, is only suitable for pure cultures, as it affords no means of separating the different bacteria. To accomplish this, Koch introduced the method of "plate culture," which consists in pouring the melted gelatine upon levelled plates of glass on which it is allowed to set, and which are then carefully protected under a bell glass from the possibilities of contamination by aerial germs. These plates have been almost superseded by the "Petri dish," a flat glass box of about 4 inches diameter with a cover, as the latter are much easier to handle. In this case the bacteria, if not too numerous, develop at separate points upon the plate, forming colonies which may be counted, and which usually consist of one species of bacterium only. By inoculating fresh tubes from these colonies and repeating the process, pure cultures are easily obtained. From the difficulty of excluding aerial germs the method is difficult in a general technical laboratory, but a modification of it ("roll culture") suggested by Esmarch, may be successfully adopted.

In this case the test-tube containing the gelatine, instead of being poured on a glass plate, is simply heated by immersion in water sufficiently warm to liquefy the solution, and is then revolved in an horizontal position so as to spread the gelatine uniformly over its sides, and at the same time is cooled by water from a tap, or by the application of ice. As in this operation the solution comes in contact with the plug of cotton-wool, which may contaminate it, and which it is apt to render impervious to air, it is advantageous to substitute for test-tubes the thin blown cylindrical bottles which have been mentioned on p. 444, in which the gelatine may be uniformly distributed by rolling in a shallow tray containing a small quantity of ice-water. The colonies will then develop upon the sides of the bottle, through which they may be examined with a low power of the microscope, or with a simple lens, to distinguish whether they liquefy the gelatine and to observe their other characteristics of growth and appearance. Portions of colonies may be withdrawn with a piece of platinum wire for the inoculation of fresh tubes.

• In some cases it is desirable, in order to obtain an approximate idea of the number of bacteria present in a water or fermenting

solution, to count the colonies which are formed; this is most readily done by partially surrounding the bottle or test-tube by a piece of black paper in which an aperture exactly 1 centimeter square has been cut with a penknife. For plate cultures or Petri dishes, cover-glasses etched with a square of 1 cm. divided into squares of 2 mm. are still more convenient where the colonies are numerous. For roll cultures squares scratched on mica or celluloid may be used. The number of colonies which can be counted with a lens on 1 cm. is determined in various parts of the tube, and the average multiplied by the whole area of the surface of the plate or tube measured in centimeters will give the number of colonies produced by the quantity of material introduced into the tube. The tube must be watched, as different species of bacteria develop with varying rapidity, and liquefying species soon cause the colonies to run together.

It usually happens, especially with liquids occurring in the tannery, that the number of bacteria in a single drop, or even in the quantity of liquid taken up by a platinum wire, is so great that the colonies are too close together and run into one another. To avoid this a sterilised tube is inoculated, its contents melted and mixed by rolling, and from the mixture another test-tube is similarly inoculated, and from this again a third. In this way, three successive dilutions are produced, one of which will probably be of the right concentration to give satisfactory results; and if a known quantity of liquid be taken, the dilution can be calculated, and from it the number of bacteria in the original liquid. For this purpose a drop may generally be reckoned as the 20th of a c.c., and if the test-tube contained 5 c.c. of solution, each dilution would be 100th of the previous one. In infecting a tube with a drop of liquid, the gelatine should be liquified before withdrawing the cotton-wool, and the tube should be held in a sloping direction, to avoid as much as possible the entrance of atmospheric dust. Where larger dilution is required sterilised water may be advantageously substituted for the nutritive medium.

The method of obtaining pure cultures with nutrient liquids is similar in principle to the above, but the dilution must be carried much further, in order that, out of a number of tubes infected, a certain proportion should not receive more than a single germ. The contents of the tubes after incubation are examined microscopically, and those taken which appear only to contain

one species ; and, for the sake of additional safety, the processes of dilution and inoculation may be repeated in a further number of tubes. As large dilution is required, it is better to use sterilised water for the purpose in the earlier stages.

Microscopic Examination of Bacteria.—Solutions containing bacteria may be examined by placing a minute drop on a glass slip, covering with a thin cover, and employing a high power objective, as described in Sect. XXIV. For the mere recognition of the presence of bacteria a good dry 6th may be sufficient, but for detailed study a good oil immersion 12th is necessary. Abbe's illuminator, or some other condenser, is preferably used for lighting, generally with a narrow aperture of the diaphragm. If bacteria are to be studied in tissues such as the skin, sections must be made as described on p. 422, and the bacteria stained.

It is frequently found that the recognition of bacteria, especially in tissues, is extremely difficult, from their minuteness and absence of very characteristic form. This difficulty can be largely overcome by the use of stains which colour the bacteria, while leaving other parts of the tissue unaffected. The bacteria generally behave to staining agents very similarly to the nuclei of more highly organised cells. When the bacteria exist in liquids it is necessary, before staining, to attach them to a cover-glass to prevent their being washed away. The cover-glasses are made absolutely clean, by heating first in concentrated sulphuric acid, then rinsing in water, washing with alcoholic ammonia, and finally drying with a linen cloth perfectly free from grease. A small trace of the liquid containing the bacteria is then spread on the glass with a platinum wire, or distributed in a thin film by pressing a drop between two cover-glasses which are separated by sliding one after the other. The glasses are then dried in a desiccator over sulphuric acid or calcium chloride, and the bacteria are finally fixed on the glass by drawing the latter, held in the fingers, with its coated face upwards, three times, somewhat slowly, through the flame of a Bunsen burner or spirit lamp. Some little experience is necessary to learn the right amount of heating to employ, too much heat disorganising the bacteria and preventing their staining, while too little fails to fix them firmly on the glass. If the liquid contains gelatine or agar-agar, it is not so readily fixed by heating, from the solubility of these substances in water ; the addition of a small quantity of white of egg renders it less liable to wash off.

The difficulty may be also overcome by exposing the preparation for a short time to the vapours of formaldehyde or paraform, which have the property of rendering gelatine insoluble.

Preparations are frequently made from plate cultures (p. 445) by pressing a clean cover-glass on the colony which it is desired to transfer, which then adheres to the glass, sometimes showing very characteristic forms. It is subsequently treated as above to fix it.

The basic aniline colours are the most important stains for bacteria; they are employed dissolved in water, either alone or occasionally with the addition of aniline and other bases. As the aqueous solutions do not usually keep well, it is frequently convenient to make saturated alcoholic solutions by shaking the powdered colour with alcohol in sufficient quantity to leave a part undissolved. These concentrated solutions are mixed with water in proportion of 1-10 or more, as may be found necessary to give the required colour. The most generally useful colours are magenta or fuchsin, methyl violet 5 B, gentian violet, methylene blue, and Bismarck brown. Staining methods are, however, now so numerous that the reader must be referred to the special text-books. A most useful book of reference is Squire's 'Methods and Formulæ' (p. 427).

The sections or the cover-glasses on which the bacteria are fixed are placed in one of these solutions in a watch glass, and remain in it ten minutes or more, until the bacteria are sufficiently coloured. The solutions are frequently employed warm, where the bacteria do not readily take the stain. Instead of water a saturated solution of aniline, made by shaking three or four grams of aniline oil with 100 cubic centimetres of water, and filtering, is frequently employed to dilute the alcoholic colour solutions. The preparation is then washed with water, which usually removes the colour from the tissue, leaving the bacteria stained, which may now be examined without further treatment, or may be dried and mounted with a drop of Canada balsam dissolved in xylene, which is preferable to chloroform, as less liable to decolorise the bacteria. For the same reason, if a clearing liquid is required, oil of cedar is preferable for the purpose to oil of cloves.

In the foregoing Section the writer is greatly indebted to the suggestions of his friend, Mr. J. T. Wood, who has been good enough both to read and to criticise the manuscript before printing, and to assist in examining the proofs.

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